INTERIM MEASURES AIR SPARGING PILOT TEST SUMMARY REPORT

Draft

Prepared for:
ASARCO Incorporated
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INTERIM MEASURES AIR SPARGING PILOT TEST REPORT

1.0 INTRODUCTION

Arsenic has been identified as the primary constituent of concern in groundwater at the Asarco East Helena plant site. Under the Interim Measures (IM) Work Plan (Hydrometrics, 1999), Asarco committed to implementing a series of interim measures designed to address arsenic releases from identified source areas and evaluate migration control measures that could be implemented as interim measures to reduce arsenic migration in groundwater from the plant site.

The IM Work Plan identified in-situ treatment of groundwater through redox controls as a potential measure for control of arsenic migration in shallow groundwater. Water quality data suggest that a portion of the dissolved arsenic in groundwater on the plant site is already being actively attenuated in the shallow groundwater system through co-precipitation/adsorption of arsenic with hydrous iron oxides/hydroxides. The IM Work Plan proposed further evaluation of air sparging as a potential means of controlling the redox state of groundwater and thus further limiting arsenic mobility.

Although testing is required to fully assess the potential feasibility of air sparging for attenuation of arsenic in groundwater at the site, it has a number of potential advantages for implementation as an interim measure. For example, air sparging could be implemented without extensive permitting and it does not require construction of large-scale treatment facilities.

Groundwater capture was also evaluated in the IM Work Plan, but was found to have limited technical feasibility as an interim measure as a result of insufficient treatment capacity at the existing water treatment plant. Extended time would be necessary for development and implementation of the additional treatment facilities needed for groundwater capture at the site boundary. While groundwater capture will be further evaluated as a potential long-term measure under the RFI, it was not considered feasible in the short-term without available capacity at the existing treatment plant.

The IM Work Plan included a scope of work to evaluate the feasibility and effectiveness of air sparging for control of arsenic migration in groundwater. Under this plan, conventional air sparging technology (injecting air into the groundwater system) was used to increase the oxidation state of groundwater and shift the arsenic redox equilibrium toward dominance by As (V) species. Arsenic is typically less mobile as As (V) than As (III). In addition, dissolved ferrous iron (Fe^{2+}) in groundwater may be oxidized to Fe^{3+}, subsequently precipitating as ferric hydroxide, and potentially binding arsenic either as a co-precipitate or as an adsorbed species.

1.1 OBJECTIVES

The primary objectives of the air sparge pilot tests were to evaluate water quality changes as a result of air sparging, and determine whether this technology has potential application as an interim measure for attenuation of arsenic in shallow groundwater. Goals of the air-sparging test were:

1. To determine if air sparging is capable of changing the arsenic redox state of groundwater and thereby increasing arsenic attenuation within the aquifer.
2. To evaluate whether air sparging is capable of achieving regulatory limits for arsenic in groundwater.
3. To identify potential design parameters for application of air sparging technology at this site.

1.2 SCOPE

Air sparge pilot testing at the East Helena Site was conducted from April 2000 through December 2002. The testing program consisted of three general phases.

1.2.1 Phase I Pilot Testing Program

The Phase I air sparging program was conducted from April 2000 through February 2001 and included the following tasks:

- Siting and design analysis to select locations for test wells and design the sparge pilot scale system. The analysis was based on IM hydrogeological data compiled in the proposed test area and presented in the IM Supplemental Groundwater Report (Hydrometrics, 2000).

- Installation of three sparge pilot scale testing wells at two locations based on a review of the IM hydrogeological data. Two locations were tested rather than one to evaluate the effects of varying geochemical conditions in the plume area. Six additional monitoring wells were also installed to supplement the existing monitoring well coverage for the testing program, and better define the area of influence for the sparge system.

- Documentation of baseline water quality at both air sparge pilot test sites, and at the existing monitoring network prior to air sparge pilot scale testing.

- Performance of air sparge pilot scale tests at two separate locations. The tests were used to evaluate the effectiveness of air sparging in groundwater that had differences in pre-test water quality.

Results of the Phase I testing program were presented in an interim measures testing report (Hydrometrics, 2001a) and are included in this Air Sparge Summary Report (see Section 2).

1.2.2 Phase II Air Sparge Testing Program

Following the completion of the Phase I testing, additional bench-scale testing was conducted from February 2001 through June 2001 to assess the feasibility for the introduction of iron to the groundwater system in the air sparging area, thereby enhancing arsenic removal. A series of batch tests and column tests were conducted with the following objectives:

1. Assess the solubility of various iron reagents in groundwater from the site.
2. Evaluate iron attenuation by site soils.
3. Evaluate the effect of varying iron concentrations on groundwater pH.
4. Evaluate the effect of iron concentrations and pH on iron/arsenic removal rates.
5. Evaluate time required for iron/arsenic precipitation.
6. Evaluate the stability of arsenic bearing iron precipitates.

Results of the Phase II Bench testing program were presented in an interim measures testing report (Hydrometrics, 2001b) and are included in this Air Sparge Summary Report (see Section 3).

1.2.3 Phase III Air Sparge Pilot Testing Program.

A Phase III pilot was conducted from September 2001 through December 2002. The objectives of this Phase of testing were to provide a more long-term evaluation of sparging, and to test iron introduction methods to enhance removal of arsenic in groundwater during air sparging. This report presents the results of Phase III testing efforts (see Section 4).

All phases of the air sparge testing are summarized Table 1-1 and are discussed below.

2.0 PHASE I PILOT TESTING

2.1 SITING ANALYSIS

A siting analysis was conducted to identify locations with favorable hydrogeologic conditions for pilot testing an air sparge system. Monitoring wells DH-24 and DH-50 were identified as the potential locations for testing, since they lie near the downgradient plant site boundary and are within the north-northeast trending arsenic plume which extends across the plant site boundary (see Figure 2-1). Monitoring well DH-50 is located at the north side of the Asarco plant property and just south of the American Chemet property fence. Monitoring well DH-24 is located about 125 feet west of DH-50 and is also near the boundary between Asarco property and American Chemet property.

Pre-test dissolved arsenic concentrations at DH-24 and DH-50 were approximately 13 mg/L. The hydrogeology of this area was examined to determine optimal locations for the air sparge pilot testing program.

2.1.1 Hydrogeology

Suitable geologic conditions need to be present to apply air sparging effectively. Typical site requirements for air sparging are:

- A minimum of 5 feet of saturated thickness.
- No fine-grained strata inhibiting the upward migration of air to the water table.
- Suitable permeabilities for air injection (1×10^{-3} cm/sec or higher).

Figure 2-2 is a detailed geologic cross-section of the northern plant site area in the vicinity of DH-24 and DH-50. In general, the subsurface stratigraphy was found to consist of a sequence of silty sand and gravel to a depth of approximately 25 feet. From approximately 25 feet to 40 feet, sandier layers were encountered at irregular intervals. Both DH-24 and DH-50 are completed in this sandy interval and existing aquifer testing data exhibit relatively high permeability for these strata.

Aquifer testing results (Asarco Consulting, 2003) indicate DH-24 has the highest hydraulic conductivity ($1x10^{-1}$ cm/sec), while well DH-50 shows a slightly lower hydraulic conductivity ($2x10^{-2}$ cm/sec). Well completion logs show the presence of a fine-grained layer at 35 feet in DH-24; however, available information did not show any indication of fine-grained strata at well DH-50. As a general rule, the deeper the air sparge well can be completed below the water table, the larger the effective radius. During seasonal low water table conditions (which typically occur in April and early May), the geology at DH-24 would provide only a few feet of saturated thickness. Thus, the area near DH-24 was not considered an optimum air sparge test site due to the limited saturated thickness of the sand aquifer and the presence of the underlying fine-grained strata. Because the presence of a fine-grained layer at DH-24 could limit the effective dispersal of oxygen through the shallower saturated strata, the area near DH-50 was selected as the primary air sparge testing site.

Although the DH-24 area was not selected for the initial air sparge test because of stratigraphic limitations, existing water quality data indicated a significant difference in water quality from DH-50. DH-24 showed higher concentrations of iron and a slightly lower pH (see Section 2.4). Because these parameters are important factors in groundwater arsenic mobility, the area near DH-24 was included as a second air sparge-testing site.

2.1.2 Groundwater Flow Conditions

Figure 2-3 shows the arsenic plume, configuration, and potentiometric contours for the shallow groundwater system in the vicinity of monitoring well DH-50. The regional groundwater flow direction and the general direction of plume migration is to the north-northwest. However, the 1999 potentiometric data indicated localized variability and suggested there could be a north-northeast flow direction in the immediate vicinity of DH-24 & DH-50. This interpretation is driven largely by the higher observed water levels at DH-24. The water level trends depicted in Figure 2-3 were confirmed by water level measurements in April 2000.

The hydraulic gradient (i) in the vicinity of DH-50 is 0.011. Based on a hydraulic conductivity (K) of 59 ft/day and an assumed porosity (n) of 30%, the average groundwater velocity (v) in the shallow groundwater system is calculated at approximately 2 ft/day ($v = K*i/n$). This is consistent with previous analyses which indicate typical groundwater flow velocities on the order of 1 to 3 ft/day at the site.

Based on the groundwater flow directions and estimated groundwater flow velocities, two locations were selected for air sparge well construction, and six locations were selected for test monitoring wells (see Figure 2-3). As described in Section 2.2.1.2 of this report, it was necessary to construct two air sparge wells (SPAR-1, SPAR-2) at the first test location near monitoring well DH-50 to ensure adequate air distribution based on the site stratigraphy at this location.

2.2 SYSTEM DESIGN AND INSTALLATION

2.2.1 Air Sparge Well Design and Installation

Three air sparging wells (SPAR-1, SPAR-2 and SPAR-3) and six sparge test monitoring wells (STW-1 through STW-6) were constructed for Phase I pilot testing purposes. Air sparging and monitoring well locations are shown on Figure 2-3 and well lithologic and construction logs are in Appendix A.

2.2.1.1 Test Well Locations

Air sparging wells SPAR-1 and SPAR-2 are located approximately 50 feet south of existing monitoring well DH-50. SPAR-3 is located approximately 125 feet to the west of SPAR-1 and SPAR-2 and approximately 25 feet south of monitoring well DH-24.

Monitoring wells (STW-1 through STW-6) were constructed near air sparge wells, SPAR-1 and SPAR-2, to evaluate the effects of air sparging on groundwater quality and determine the effective zone of influence. Well STW-1 is located 75 feet south and hydraulically upgradient of the air sparge wells and was installed to evaluate background water quality. Wells STW-2 through STW-6 are located north of the air sparge wells to evaluate groundwater quality.

hydraulically downgradient of the sparging system. Downgradient monitoring wells were sited to evaluate the anticipated zone of influence from the air sparging system. A rule of thumb for estimating the potential radius of influence is two times the injection depth (depth below the water table). A radius of influence of approximately 18 feet was initially anticipated assuming the air sparge well screen was located 9 feet below the water table surface. The actual radius of influence was evaluated during operation of the air sparging system and is described in Section 5.

2.2.1.2 Test Well Lithology

Subsurface soil samples were collected using 2-inch or 3-inch diameter split spoon samplers. Because of problems recovering samples in the beginning of the program due to the abundant gravels, a larger 3-inch diameter sampler proved to be more effective for sample collection. Grab samples were also collected at the ground surface and in some instances from drill rig cuttings (at the discretion of the field geologist.) Borehole samples were examined for lithology, grain size, texture, and color. Following field lithologic analysis, soil samples were archived and are available for any future analytical evaluation.

Since the air sparging wells and test monitoring wells were located relatively close together for pilot testing purposes, it was possible to obtain detailed descriptions of the testing area stratigraphy during the well drilling process. Based on lithologic well logs in Appendix A, detailed stratigraphic cross-sections were prepared (see Figure 2-4). As the cross-sections show, the stratigraphy of the pilot test area generally consists of a heterogeneous mixture of coarse-grained alluvial gravel, sand and cobbles with discontinuous layers of silty sand and occasional discontinuous silty clay layers. These variations in texture appear to be very localized and reflect a highly heterogeneous stratigraphy in the testing area.

As described in Section 2.1.1, the location for the first air sparge test was selected because existing information from Well DH-50 showed the presence of a saturated sand layer without the fine-grained silty clay layers that were noted at DH-24 (see DH-50, Cross Section B-B', Figure 2-4). Although available stratigraphic information did not indicate the presence of fine-grained strata at monitoring well DH-50 (see Section 2.1.1), a fine-grained silt layer was observed during the drilling of air sparge well SPAR-1. Since the presence of this layer was a cause of the same concerns for the area near DH-24 (i.e., the fine-grained layer could limit the ability to distribute oxygen in shallower saturated coarse-grained strata), a second air sparge well, SPAR-2, was constructed adjacent to SPAR-1. The original design objective for SPAR-2 was to complete the well above the fine-grained layer that was discovered at SPAR-1. However, as shown in Cross Section B-B' (Figure 2-4), even though SPAR-2 is located only about 5 feet to the west of SPAR-1, drill core samples did not show the presence of the fine grained layer noted at SPAR-1. As the cross sections in Figure 2-4 show, this pattern of heterogeneous stratigraphy was also observed during air sparge test monitoring well drilling and sampling.

2.2.1.3 Test Well Construction and Development

Air sparge well completion details are in Figures 2-5 and 2-6 and typical test shallow monitoring well construction details are in Figure 2-7. Similar to past monitoring well construction in the area, the air sparging wells and sparge test monitoring wells were drilled using a Mobile B-61/ODEX drilling rig to allow drilling through cobble and boulder strata that overlie the target completion zone (saturated sand). Previous monitoring well drilling in this area required use of an ODEX or conventional air rotary drilling system due to the presence of coarse gravels and large basalt cobbles.

The sparge wells were constructed using 2-inch flush-threaded schedule 40 polyvinyl chloride (PVC) pipe and two to three foot of factory slotted (0.010 slot) well screen, and were sand packed and grouted to meet Montana monitoring well standards.

The total depth for the air sparge wells ranged from 40 to 41 feet below ground surface (bgs), and the screen interval ranged from 35 to 40 feet bgs. A target depth of 40 feet for the air sparge wells was chosen because the top of the water table was measured at a depth of 31 feet bgs on April 18, 2000 at well DH-50. A depth of 40 feet maximizes the effective amount of saturated interval above the sparge point. Table 2-1 presents a summary of air sparge well construction details.

Sparge test monitoring wells were also completed with 2-inch schedule 40 PVC casing with flush joints and threaded couplings. Water bearing intervals were screened with 0.010 factory slot screen, and 2-inch schedule 40 casing. Five feet of well screen was set 1-2 feet below the seasonally low water table. The screens and sand packs were not allowed to intersect the water table to prevent pathways that would allow short-circuiting of air to the unsaturated zone.

The sand packs were installed to one foot above the well screen using 10/20 silica sand. The annular seal above the sand pack consisted of 2 to 3 feet of bentonite chips overlain by bentonite grout to ground surface. The sand pack and annular seal were installed as the ODEX casing was incrementally removed from the borehole. Each monitoring well was completed with a steel protective casing and locking lid.

The air sparging wells and monitoring wells were drilled by Hydrometrics using a B-61 mobile drilling rig. Hydrometrics had a licensed Montana monitoring well constructor present during drilling and well construction operations.

Following well completion, piping from the air compressor was connected to the air sparge well with a T-connection to allow access to the well. Details for the aboveground air sparge system design are presented in Section 2.2.2 of this report.

2.2.2 Air Sparge System Design

2.2.2.1 Air Compressor Selection

Potential airflow and air pressure requirements for air sparging were calculated based on site-specific parameters to determine specifications for a compressor. Recommended airflow requirements are 5 to 10 cfm (cubic feet per minute) per well (WDNR, 1993). Air pressures required to achieve these flow rates are a function of the water depth, and aquifer permeability. Calculations are outlined below.

Calculated Air Pressure Required for Air Sparging

Pressure of Injection (P_i) = $H_i + P_r$

where: (H_i) = Depth of Water Column = 8 ft (assumed height of water above screen)

(P_r) = Release pressure due to frictional losses and the capillary resistance of the formation = 2.3 feet of water (1 psi) for every 4 feet of sand (representative value for a medium grained sand - Nyer & Suthersun, 1993)

(P_r) = 4.6 ft

P_i = 8 ft + 4.6 ft = 12.6 ft **P_i = 5.5 psi**

The calculated air pressure necessary for air sparging is 5.5 psi. Actual air pressures will vary depending on the actual geologic conditions and completion depth at the air sparging site. Maximum air pressures were also calculated to identify the upper pressure range where hydraulic fracturing of the formation may occur. These calculations are based on WDNR (1993) design guidelines, which indicate that the pressure should not exceed the weight of the soil column. Maximum air pressure calculations assume a soil particle density of 2.7, a porosity of 40% (conservative estimate) and a 5 psi safety factor to avoid over pressuring the well.

Calculated Maximum Air Pressure

Weight of Soil	= 40 ft * 2.7*0.6*62.4 lbs/ft = 404 lbs/ft^2
Weight of Water	= (40-29.5) ft 0.4*62.4 lbs/ft = 262 lb/ft^2
Total	= 4044 + 262 = 4306 lbs/ft^2 = 29.9 psi
With safety factor	= 29.5-5 **= 24.5 psi**

Based on these results, a Gast 2567, 1.5 HP rotary vane, oil-less compressor was selected. This compressor uses 115 volt single phase power which is available at a power pole on the site. The compressor produces airflow output of up to 21 cfm at 20 psi. This is a sufficient capacity to allow for uncertainty in site conditions and provides a suitable flow and pressure range for operational testing.

2.2.2.2 Piping and Instrumentation

A schematic layout of the air sparge system is shown in Figure 2-8. Two-inch diameter schedule 40 PVC piping was used to connect the air sparge well and the compressor. Airflow to the air sparge well was cycled to maximize diffusion of oxygen in groundwater. A timer was used to cycle the compressor. Injection times were determined based on initial start-up testing by evaluating the time required for maximum water level response in observation wells (described in Section 2.3.1). Other instrumentation included:

- A check valve between the well and compressor to prevent water from surging in the well when the system is shutdown;
- A ball valve to adjust airflow rates;
- A pressure gage; and
- An in-line metered flow restrictor to monitor and control airflow rates.

2.3 AIR SPARGE PILOT TEST METHODOLOGY

2.3.1 System Start-up

An initial start-up evaluation was made after system installation and prior to conducting an extended pilot test. The system was briefly started up to adjust the airflow and monitor the water level response in the groundwater system. Water levels in the outlying wells, and airflow and air pressure in the air sparge system were monitored during this start-up test to evaluate cycling periods for operation of the sparge system.

An air leak developed in a fitting at the SPAR-1 sparge well during start-up testing. As a result, air was injected only through the SPAR-2 sparge well. Airflow monitoring indicated that the SPAR-2 well was capable of injecting air at the desired flow rate of 5 to 10 cfm at acceptable operating pressures (8 to 14 psi). Air pressures gradually increased for the first 20 minutes of the test and flow rates gradually decreased (Figure 2-9). After 20 minutes of operation, pressure rates began to stabilize at approximately 14 psi and airflow rates at 5 cfm (cubic feet per minute). A water level response was observed in all the sparge monitoring wells during start-up testing. Water levels, like airflow rates, stabilized after about 20 minutes of operation (see Figure 2-10). Based on this response, the sparge system was set to cycle at 15-minute intervals. The cycling is designed to minimize the potential for preferential flow paths to become established and maximize dispersion of the air in the groundwater system.

2.3.2 Phase I Pilot Test

The Phase I sparge pilot test began on May 23, 2000 using the SPAR-2 test well. The test was designed to evaluate the influence of sparging on groundwater redox conditions and metals concentrations. On June 15, 2000, SPAR-1 was also put into operation and both SPAR-1 & SPAR-2 were used as sparge wells to increase airflow rates. On June 29, 2000, the air sparge cycling intervals were fine-tuned. Air injection cycles were adjusted to have the system cycle on for 15 minutes and then off for 45 minutes. This was done to evaluate whether shorter injection cycles would still maintain adequate dissolved oxygen levels while minimizing potential disturbances to the physical flow field. Previous investigators and field tests have shown that short injection cycles followed by longer recovery cycles are often more effective. A primary factor for this phenomenon is the change in water permeability of the aquifer as void space is replaced by air during the air sparge process (NWWA, 2000). Longer recovery cycles allow more dispersion into the aquifer and can enhance the effectiveness of oxygenation of the groundwater system.

Testing at SPAR-1 and SPAR-2 was completed on August 9, 2000. A second sparge test was initiated at the SPAR-3 well on the same day. The purpose of this second test was to evaluate the effects of higher ambient iron concentrations on arsenic removal rates. As discussed in

Section 2.1, and in further detail in Section 2.4.1, dissolved iron concentrations are much higher in the vicinity of SPAR-3 and DH-24 compared to the SPAR-1 & 2 area.

2.3.2.1 Operational Parameters

The target air injection rates for the air sparge test were 5 to 10 cfm. The actual air injection rates and injection pressures achieved during the pilot scale tests are shown in Figure 2-11. As indicated in the graphs in Figure 2-11, airflow rates were initially around 7 cfm at the first sparge site and gradually decreased to 5 cfm within a few weeks of operation. Air injection pressures at SPAR-2 increased over this same period from 7 to 13 psi. These rates are within the original design parameters for the system, but slightly lower than the design estimates.

On June 15, 2000, the second sparge well (SPAR-1) was turned on to provide increased airflow. The air injection rates increased to almost 16 cfm with the addition of the second sparge well and sparge injection pressures dropped to 5-7 psi. These flow rates and injection pressures are more consistent with the operational parameters estimated in the original design calculations. The well completion logs (Appendix A) indicate SPAR-1 is completed in a medium-grained sand unit, which is the type of material assumed in the original design analysis. The well log for SPAR–2 shows finer sand in the completion zone.

Some operational data were also collected at the SPAR-3 site. However, the logistics of collecting operational data were more difficult at this site due to the fact that the system needed to be shutdown to sample the SPAR-3 well. As a result, there are less operational data from this test. Airflow pressures and injection rates are shown in Figure 2-11. Airflow at SPAR-3 ranged from 8 to 10 cfm with injection pressures of 8 to 14 psi. SPAR-3 is screened in a silty sand and gravel unit.

The heterogeneous geology in this area may account for the variability in sparge rates, as well as some of the variability in water quality effects at the observation wells. Despite this variability, the sparging produced fairly well distributed effects in the downgradient area.

2.3.2.2 Water Quality Monitoring

Groundwater quality sampling was conducted prior to the test and during air sparging to assess the effects of air sparging on groundwater chemistry, and to estimate the radius of sparging influence. The groundwater sample collection and monitoring plan is summarized in Table 2-2.

Prior to air sparging, all IM and RI/FS monitoring wells were sampled as part of the regular semi-annual monitoring at the plant site during the week of April 25, 2000. The sample analyses included field parameters (F), metals (M), commons ions (C), and arsenic speciation (A) as shown in Table 2-3. All of the newly installed sparge monitoring wells were sampled on May 10, 2000 (after well development) for the same set of monitoring parameters (F, M, C, A). DH-50 and all of the sparge monitoring wells were sampled a second time on May 18, 2000 to provide a second round of pre-test monitoring data for field parameters and metals (F, M).

The monitoring schedule for the Phase I air sparge pilot tests is summarized in Table 2-2 and includes sampling dates. The sampling parameters for SPAR-1 and 2, and SPAR-3 are listed in Table 2-3. Samples were sent to Asarco's Salt Lake City Technical Services laboratory for expedited analysis.

Eleven monitoring rounds were conducted over the 13-week duration of the Phase 1 SPAR-1 and 2 testing program. Wells STW-1, STW-2, STW-3, STW-4, STW-5, STW-6, and STW-7 were monitored during the first three rounds of the SPAR-1 and 2 pilot test program. DH-24, DH-50, and DH-60 were added during the fourth round in order to evaluate the full radius of influence of air sparging. During the fifth through the eighth round, only the original wells (STW-1, STW-2, STW-3, STW-4, STW-5, STW-6 and STW-7) were sampled. The final round of the SPAR-1 and 2 pilot test program included all previously sampled wells with the exception of DH-50 and the addition of SPAR-3.

SPAR-3, DH-24, and EH-60 were monitored during the Phase 1 SPAR-3 pilot test. Monitoring wells from the first air sparge location (see Table 2-2) were also tested periodically to determine post-sparging water quality effects from the SPAR-1 and 2 testing program.

2.3.2.3 Sampling Protocol

The air sparge system was shutdown during well sampling. Sampling was then conducted following the protocol established in the IM work plan with two modifications:

1. Additional purging was performed to minimize the potential for extraneous water quality effects due to potential channeling of air to the sand pack of a well. Airflow may channel through discrete flow paths to the sand pack of a well. In such a case, water in the sand pack may become more oxygenated than in the surrounding aquifer. This is primarily a concern for wells within the immediate zone of influence of the sparge well. For water quality sampling and determination of sparging effects on groundwater chemistry, it was important to ensure that water collected from wells was truly representative of general groundwater conditions (as opposed to conditions within the borehole and associated sandpack). Therefore, purging volumes were calculated based on the estimated quantity of water within both the well and the sandpack. Approximately three borehole volumes (well plus sandpack) of water were removed prior to sampling.

2. Field parameters (specific conductance, temperature, pH and dissolved oxygen) and iron speciation were measured in the field. Iron speciation measurements in groundwater samples (concentrations of Fe^{2+} and Fe^{3+}) were collected using a field-portable HACH DR2000 spectrophotometer. Ferrous iron (Fe^{2+}) and total iron (Fe(tot)) are measured independently, and Fe^{3+} is calculated as the difference between total and ferrous iron, or [Fe(tot) - Fe^{2+}]. The analytical procedure for colorimetric iron speciation measurements is detailed in the DR2000 Methods Manual, and is summarized in Appendix B.

2.4 PHASE I PILOT TESTING RESULTS

2.4.1 Pre-test conditions

Field parameters and laboratory analytical results from the pre-test sampling rounds are shown in Table 2-4. Dissolved oxygen (DO) results from pre-test monitoring rounds show DO concentrations in groundwater of approximately 1 mg/L in all of the wells prior to sparging.

Dissolved arsenic concentrations in test wells prior to sparging ranged from 13 mg/L to 50 mg/L, with higher concentrations in upgradient wells and lower concentrations downgradient. Arsenic speciation data showed a ratio of arsenic III (As^{3+}) to arsenic V (As^{5+}) in groundwater between 1 and 10. The wells with higher arsenic concentrations (STW-1 and STW-4) showed higher As^{3+}/As^{5+} ratios.

Dissolved iron concentrations were very low to non-detectable in most of the monitoring wells at the first test site (Sparge 1 and Sparge 2) with the exception of STW-4 which had a pre-testing concentration of approximately 0.4 mg/L dissolved iron. Significantly higher iron concentrations were present immediately to the west, in the second test area (SPAR-3 area). Both SPAR-3 and DH-24 showed dissolved iron concentrations of approximately 12 mg/L in pre-test monitoring. In general the higher iron concentrations at these locations are accompanied by slightly lower pH (about ½ to 1 pH unit).

2.4.2 Phase 1 Testing At SPAR-1 and SPAR-2

Air sparging at the first pilot test site (SPAR-2) was initiated on May 23, 2000. Field parameters and laboratory analytical results from the testing are summarized in Figures 2-12 and 2-13. Tabulated results are included in Appendix C.

Following start-up of the sparge system, an immediate increase in dissolved oxygen was observed in the first downgradient row of monitoring wells (see STW-2 and STW-3 in Figure 2-12). This increase in dissolved oxygen was accompanied by a decrease in the As^{3+}/As^{5+} ratios (Figure 2-13). However, there was no evidence of a change in dissolved arsenic concentrations at any of the wells at this point in the test. These results indicate the sparge system was effectively converting As^{3+} to the more oxidized As^{5+} state.

Increases in DO were observed in additional downgradient wells (STW-4, STW-5, STW-6 and DH-50) after approximately 6 weeks of testing. As with the first row of monitoring wells (STW-2 and STW-3), the downgradient wells also showed a corresponding decrease in the As^{3+}/As^{5+} ratios, without evidence of a decrease in dissolved arsenic concentrations except at monitoring well STW-4. Concentrations of dissolved iron in this well had started to decrease and there appeared to be a corresponding decrease in dissolved arsenic concentrations.

By the 10th week of testing, dissolved oxygen concentrations in most of the monitoring wells appeared to be stabilizing and virtually all of the wells had significantly lower concentrations of As^{3+}. However, the wells showed no change in dissolved arsenic with the exception of STW-4. Dissolved arsenic in STW-4 decreased approximately 30% from 40 mg/L to 28 mg/L. During this same period, dissolved iron (Fe^{2+}) at STW-4 decreased from 0.7 mg/L to approximately 0.1 mg/L. DH-50 also showed a slight decrease in dissolved arsenic concentrations, from 11 mg/L to 8 mg/L. Dissolved iron concentrations in DH-50 were less than detection throughout the test.

The first pilot test was stopped on August 9, 2000 after 11 weeks. After sparging ended, dissolved oxygen concentrations gradually returned to pre-test levels. As^{3+}/As^{5+} ratios, however, remain significantly lower than initial conditions. Dissolved arsenic concentrations at STW-4 returned to near pre-test levels after approximately 8 weeks. However, concentrations remain below pre-test levels despite a slight increase in upgradient concentrations during this same period as evidenced by water quality trends at STW-1.

In summary, the primary water quality change observed during the first pilot test was an increase in DO concentrations in shallow groundwater and oxidation of arsenic from As^{3+} to the As^{5+} state. Significant dissolved arsenic reductions, however, were only observed in STW-4 where iron was initially present in groundwater. A slight decrease in dissolved arsenic concentrations was also observed at DH-50, the furthest downgradient well. But in this case, iron removal was not a factor since dissolved iron concentrations were below detection at this well. The zone of influence of the sparge system based on these test results is discussed in Section 2.4.4.

2.4.3 Phase I Testing at SPAR-3

Air sparge testing was initiated at the SPAR-3 site approximately 125 feet to the west of the first location, SPAR-1 and SPAR-2, on August 9, 2000. Groundwater at this location has similar dissolved arsenic concentrations to wells at the first sparge site, but significantly higher dissolved iron. Dissolved iron concentrations at SPAR-3 and DH-24 were approximately 12 mg/L prior to testing.

Field parameters and laboratory analytical results from the testing are summarized in Figures 2-14 and 2-15. Tabulated results are included in Appendix C.

Results from the first monitoring round showed only slightly elevated DO at the sparge well (SPAR-3); however, there was a significant decrease in dissolved iron concentrations. The operation of the sparge system was interrupted sometime between the middle and end of August 2000 due to a power surge. The system was restarted on August 31, 2000. After this second start-up, DO showed a sharp increase at SPAR-3 and dissolved iron concentrations dropped to less than 0.5 mg/L. There was also a sharp drop in dissolved arsenic concentrations at the sparge well. Dissolved arsenic concentrations were reduced approximately 90%, decreasing from 25 mg/L to approximately 3 mg/L.

Over the next seven weeks of operation, similar arsenic trends were gradually observed in downgradient well DH-24. Dissolved arsenic appeared to stabilize at concentrations similar to SPAR-3. While a decrease in dissolved iron concentrations (Fe^{+2}) and As^{3+}/As^{5+} ratios indicate some increase in the oxidation state of groundwater at DH-24, there was no observable increase in dissolved oxygen.

Downgradient well EH-60, located in East Helena, showed various water quality changes during the test period. However, it was difficult to determine if any of the observed water quality trends at EH-60 were directly related to system operation. In addition, a local City of East Helena water supply pipeline leak on Pacific Street had known water quality effects during this period (Asarco Consulting Inc, 2003). Testing at SPAR-3 was shutdown on November 3, 2000 after nine weeks of operation due to an electrical problem.

2.4.4 Discussion of Water Quality Results

Baseline monitoring results show that under ambient conditions dissolved oxygen (DO) concentrations in groundwater are relatively low, typically about 1 mg/L. Dissolved arsenic is present in groundwater in the sparge area in the form of As^{3+} (arsenite), and As^{5+} (arsenate). Upgradient of the SPAR-3 test site, As^{3+} (the more reduced form of arsenic) is the dominant species. However, the oxidized form of arsenic, As^{5+}, gradually becomes dominant as groundwater flows downgradient. Correspondingly, pe values (oxidation/reduction potential) for groundwater calculated from As^{3+}/As^{5+} ratios increase as groundwater flows downgradient. These trends in groundwater chemistry between STW-1 and DH-50 (see Figure 2-16) indicate that groundwater is undergoing a change in redox state in this area even prior to sparging. Figure 2-16 also shows a decrease in overall dissolved arsenic concentrations along this flow path (from 46 mg/L at STW-1 to 11 mg/L at DH-50). The concurrent decline in dissolved arsenic concentrations with increase in oxidation state of groundwater pe suggest a relationship between arsenic attenuation and redox state.

Although arsenic co-precipitation with iron hydroxides is believed to be a significant factor in arsenic attenuation in groundwater on portions of the plant site, groundwater in the vicinity of these wells has little or no detectable iron. The primary mechanism for arsenic removal may be adsorption of arsenic to iron oxides in the aquifer or other mineral surfaces. Typically arsenic is more readily adsorbed as arsenate than as arsenite; therefore, the purpose of air sparge testing in this area was to examine whether increasing DO concentrations in groundwater could oxidize arsenic to the more readily attenuated form.

As previously discussed in Section 2.4, dissolved iron concentrations in groundwater are significantly higher and pH values are lower in the SPAR-3 area immediately to the west of the first SPAR-1 and SPAR-2 test site. Measurements confirm that essentially all of the dissolved iron is present in groundwater as the reduced form of iron, ferrous iron (Fe^{2+}). Upon oxidation to ferric iron (Fe^{3+}), iron becomes very insoluble and iron oxides/hydroxides typically precipitate and are removed from solution. Because of the presence of ferrous iron in groundwater in this area, arsenic may be amenable to removal by co-precipitation of arsenic with iron oxides/hydroxides under the proper redox conditions. Prior to testing, there was little evidence of active iron removal in the immediate area of the air sparge wells. The SPAR-3 air sparge pilot test examined whether increasing DO concentrations in groundwater would effectively remove iron and result in higher arsenic attenuation rates as a result of arsenic co-precipitation with iron.

Data collected during the air sparge tests were examined to evaluate the following issues:

1. The amount and extent of DO effects in the shallow groundwater system.
2. Whether increasing the DO effectively changed the redox state of iron and arsenic.
3. Effects of increased DO and redox on dissolved arsenic and iron concentrations.
4. Post-operational water quality changes.

Air sparging test results clearly indicate that sparging was effective at introducing DO into the shallow groundwater system at the sparging wells and in surrounding groundwater. Prior to sparging, DO concentrations in all wells were approximately 1 mg/L. Soon after the start of sparging, DO concentrations increased to near saturation levels (8 to 12 mg/L) in groundwater in the immediate vicinity of the sparge wells. At the SPAR-1 & 2 test site where monitoring wells were fairly closely spaced, the test data show a 20 foot wide zone of increased dissolved oxygen (at 2-3 mg/L) extending downgradient of the sparge wells (Figure 2-17). In contrast, no DO changes were evident in downgradient well DH-24 at the SPAR-3 test site. Since changes in arsenic speciation and dissolved arsenic were evident at DH-24, it is likely that the oxygen was consumed in redox reactions before reaching DH-24.

Sparging test results clearly demonstrate that increasing the DO content of groundwater by sparging causes oxidation of arsenic in groundwater. As indicated, both test sites showed a change in arsenic speciation from dominantly As^{3+} prior to the test, to dominantly As^{5+} during and for a time after the test. This redox change was most evident at the first test site (SPAR-1&2) where virtually all of the arsenic in all of the wells was converted to As^{5+} by the end of the test (see Figure 2-18). The area showing redox changes (as defined by an arsenic speciation change) was considerably wider than the DO plume (see Figure 2-17).

Arsenic speciation changes were also evident in the sparge well at the second test site (SPAR-3) where the As^{3+}/As^{5+} ratio decreased approximately 10,000 fold. There are not enough wells at SPAR-3 to define the areal extent of redox changes in downgradient groundwater. However, it may be somewhat smaller in the SPAR-3 area since more oxygen is being consumed in redox reactions with iron. This appears to be the case at DH-24 where redox changes are less pronounced than wells at similar distances near the SPAR-1& 2 test site.

Increasing DO contents and oxidation of arsenic in groundwater only produced an appreciable reduction in dissolved arsenic concentrations at wells where dissolved iron was initially present in groundwater. At the first test site, dissolved iron concentrations were low (< 1 mg/L) throughout the test and dissolved arsenic decreases were modest (approximately 0 to 40 percent) in all wells. At the second test site, dissolved iron concentrations were higher (12 mg/L) prior to the test and dissolved arsenic decreases during the test were higher (up to 91 percent in the sparge well). While arsenic removal was greatly enhanced by sparging in the presence of iron, the concentrations of dissolved arsenic remaining in groundwater still exceed water quality standards. Arsenic removal at SPAR-3 appeared to be limited by depletion of dissolved iron in groundwater. Further reductions in dissolved arsenic concentrations by sparging may be possible if the initial concentrations of dissolved iron in groundwater are increased.

The rapid change in iron and arsenic concentrations with increases in DO is characteristic of co-precipitation of arsenic with iron hydroxides. The amount of arsenic removal observed during the tests, however, cannot be accounted for exclusively by iron-arsenate precipitation reactions. Assuming that iron and arsenic are oxidized by the sparge system, and are thus present as Fe^{3+} and $H_2AsO_4^-$ immediately downgradient of the sparge system, any precipitation of iron-arsenic solids would likely form compounds such as $FeAsO_4 \bullet 2H_2O$ (Scorodite). The stoichiometric formation of this mineral would result in removal of iron and arsenic from solution at a mass ratio of about 0.74 (i.e., the ratio of iron removed in mg/L to arsenic removed in mg/L). Calculation of removal ratios at wells STW-4 and SPAR-3, where iron and arsenic removal from groundwater has been observed, results in ratios of 0.03 at STW-4 and 0.45 at SPAR-3. The amount of arsenic removed at these wells is, therefore, greater than can be accounted for by a *simple* iron arsenate precipitation reaction. The additional arsenic removal is likely through incorporation in other compounds (entrapment within iron oxides) or adsorption to iron oxides or other surfaces.

Monitoring data collected at the first test site (SPAR-1 and SPAR-2) after the cessation of sparging indicate that the majority of sparging effects are temporary and of moderate duration. Dissolved oxygen concentrations generally had decreased to background levels (about 1 mg/L) within approximately two months after sparging ceased. Ratios of As^{3+}/As^{5+} in groundwater also increased after sparging ceased, indicating a return to more reducing conditions in groundwater. The increases in As^{3+}/As^{5+} ratios, however, are slower than would be expected based on the changes in DO concentrations.

Three months after sparging ceased, As^{3+}/As^{5+} ratios in groundwater remained lower (more oxidized) than pre-sparging conditions. Corresponding with the return of DO concentrations and As^{3+}/As^{5+} ratios to pre-sparging conditions, arsenic concentrations have also increased to near pre-sparging conditions. In particular, post-sparging data from STW-4 show a gradual return of arsenic to near pre-test concentrations in the three-month period following the test.

It is difficult to establish the extent to which the increase in groundwater arsenic concentrations results from remobilization of arsenic. The increase in arsenic concentration may simply be due to flow of untreated water back into the area from up-gradient sources. The timing of post-operational water quality changes is consistent with groundwater flow rates of approximately 2 feet per day. Dissolution experiments suggest that only a small fraction of the iron-arsenic precipitates will dissolve back into the solution. Adsorbed arsenic may be more susceptible to remobilization, particularly if there are changes in pH or redox conditions.

3.0 PHASE II BENCH SCALE TESTING

3.1 BENCH SCALE TESTING PROGRAM

Bench scale testing was conducted to evaluate potential methods for introducing iron and optimal concentrations for treatment. Typical reagents used to treat arsenic include ferric and ferrous salts such as ferric chloride and ferrous sulfate. Bench scale tests were conducted to assess alternate iron sources and Fe:As ratios for optimal arsenic removal. Bench scale tests were also used to better evaluate relative reaction rates and how they may influence injection scenarios.

A series of batch tests and column tests were conducted with the following objectives:

1. Assess the solubility of various iron reagents in groundwater from the site.
2. Evaluate iron attenuation by site soils.
3. Evaluate the effect of varying iron concentrations on groundwater pH.
4. Evaluate the effect of iron concentrations and pH on iron/arsenic removal rates.
5. Evaluate time required for iron/arsenic precipitation.
6. Evaluate the stability of arsenic-bearing iron precipitates.

3.2 BENCH SCALE TESTING RESULTS

The Phase II Bench-Scale Testing results are in Appendix D. Table 1 of Appendix D presents a summary of the bench-scale test results, including a brief summary of the objectives, procedures, results and conclusions for each test. Additional tables and graphs are attached in Appendix D presenting supporting data. The bench scale test showed that:

1. Ferrous sulfate appears to be an acceptable reagent. It is soluble in groundwater with only small amounts of iron precipitating after initial dilution in groundwater. Adding a small amount of reducing agent (sodium hydrosulfite) helped reduce precipitates that might eventually result in plugging of the injection well.

2. The site soils have a high iron adsorption capacity under ambient redox conditions. This will slow the dispersion of any introduced iron into the groundwater system. Low pH reduces iron attenuation rates (i.e., iron becomes more mobile as pH decreases).

3. Reagent dosages to yield iron concentrations of 200 mg/L or greater began to significantly decrease the pH of the mixed reagent/groundwater solution (pH<6).

4. 10% to 90% of arsenic was removed during sparging when dissolved iron was added to groundwater. This was similar to field results from Phase I testing. Higher initial iron concentrations produced lower arsenic concentrations after sparging. However, iron concentrations higher than 200 mg/L depressed the pH and resulted in a decrease in the rate of arsenic removal.

5. Reaction rates were relatively rapid. Increases in the duration of air sparging beyond 24 hours produced only minor additional arsenic removal.

6. When soil from a test column was leached, approximately 12% of the adsorbed arsenic was remobilized.

Based on these results, it was concluded that injection of ferrous sulfate followed by air sparging may produce desirable results. However, pH effects and attenuation of iron in the soils will need to be considered.

4.0 PHASE III AIR SPARGE TESTING PROGRAM

The Phase III Pilot Test program was developed and implemented to further evaluate the potential of air sparging as a control interim measure for arsenic migration. Development of this program was based on the data collected as part of Phase I (air sparging field tests) and Phase II (bench scale tests), review of relevant literature, and consultation with EPA technical personnel. General elements of the Phase III program consisted of the pulse operation of sparge wells SPAR-1, SPAR-2 and SPAR-3 and the introduction of dissolved iron into the shallow aquifer. This program consist of the following general steps.

1. Optimization of air sparging operational parameters through examination of Phase I Pilot Test Data.

2. Review of air and water permeability characteristics, and evaluation of design alternatives. Phase I data suggested the effectiveness of oxygen distribution could be enhanced by well spacing optimization and screen placement design. Effectiveness may also be improved by a longer pulsing approach that allows more "down time" for a more complete recovery of the aquifer from physical effects of air sparging (elevated water levels and reduced aqueous permeability).

3. Development of iron introduction methods into the groundwater system to test the potential effectiveness to enhance arsenic removal. Existing data suggest an approach that consists of the introduction of dissolved iron into the shallow aquifer upgradient of the present sparge sites could result in enhanced removal of arsenic during air sparging. The development of iron introduction methods considered:
   - Bench scale testing results to evaluate potential methods for introducing iron and optimal concentrations for treatment.
   - Evaluation of geochemical effects of iron introduction into the aquifer system. Of particular concern is the potential for chemical precipitation and plugging of well screens before the iron can be distributed through the aquifer system.

- Evaluation of the transport of dissolved iron once it was introduced in the subsurface aquifer. This evaluation included the use of groundwater flow and transport routines to simulate the transport of an artificial iron plume to the sparge system. The evaluation also considered the use of additional air or water injection points up-gradient of the sparge test area to route the artificial iron plume to the sparge testing area.

4. Development of the Phase III monitoring well design spacing, completion, and testing analytical parameters. This development included:
   - Installation of an iron injection point (STW-7)
   - Installation of additional monitoring wells (STW-8 and STW-9) downgradient of the iron introduction point (STW-7) to evaluate the geochemical effects of introduced iron in the aquifer, and to establish transport rates and direction to the SPAR-1 and 2 testing area.

4.1 MONITORING AND INJECTION WELL INSTALLATION

One iron injection point well (STW-7) and two sparge test monitoring wells (STW-8, and STW-9) were constructed as part of Phase III testing purposes. The location of these three wells is show on Figure 2-3 and well lithologic and construction logs are in Appendix A.

Iron injection point well STW-7 is located approximately 33 feet north of monitoring well STW-1. Monitoring well STW-8 is located approximately 30 feet north of STW-7 and approximately 12 feet south of sparging well SPAR-1. Monitoring well STW-9 is located approximately 35 feet north of sparging well SPAR-2. Monitoring wells STW-8 and STW-9 were constructed hydraulically downgradient of the iron injection point well STW-7 to evaluate the geochemical effects of iron injection on downgradient water quality.

Similar to past monitoring well construction, the sparge test monitoring wells were drilled using a Mobile B-61/ODEX drilling rig to allow drilling through cobble and boulder strata that over lie the target completion zone (saturated sand). Subsurface soil samples were collected as grab samples and by using a 3-inch diameter split spoon sampler. Borehole samples were examined for lithology, grain size, texture, and color.

The injection point well and sparge test monitoring wells were constructed using 2-inch flush-threaded schedule 40 polyvinyl chloride (PVC) pipe, factory slotted (0.020 slot) well screen, and were sand packed and grouted to meet Montana monitoring well standards. Typical test monitoring well construction details are shown in Figure 2-7.

Total drilling depth for the injection well STW-7 was 40 feet. STW-7 was completed across the water table with 15 feet of well screen from 25 to 40 feet bgs. Monitoring wells STW-7 and STW-8 were also drilled to a total depth of 40 feet and were screened from 35 to 40 feet bgs. Five feet of well screen was set several feet below the water table for wells STW-8 and STW-9. Table 2-1 presents a summary of construction details for all sparge test wells.

4.2 SPARGE SYSTEM DESIGN AND OPERATION MODIFICATIONS

4.2.1 SPAR-3 Startup and Operation

Phase III air sparging pilot testing was initiated October 11, 2001 (see Table 1-1). Phase III testing included concurrent sparge operation of the SPAR-1 & 2 system, and the SPAR-3 system. The purpose of concurrent operation was to evaluate long-term groundwater chemistry changes at SPAR-3 where ambient dissolved iron was present in groundwater, relative to the long-term effectiveness at SPAR-1&2 where ambient dissolved iron was lacking and where iron concentrations may be enhanced by the injection of iron into the groundwater system.

In order to facilitate concurrent sparge testing operations, a duplicate compressor was installed for the SPAR-3 system. Both compressors were identical and were a Gast 2567, 1.5 HP rotary vane, oil-less compressor. Contrary to Phase I testing, both compressors were re-wired to run on 230 volts which allowed more efficient use of electrical power. Air flow of both compressors were run at flow rates of 5 to 10 cfm at 8 to 14 psi. For Phase III testing, the system was set to run a 15 minute injection cycle followed by a 1 hour/45 minute off-cycle. Based on review of Phase I data and other sparge efforts in the literature, longer off-cycle time was expected to minimize the potential for preferential flow paths to become established and allow a good dispersion of the air in the groundwater system.

4.2.2 Iron Injection

Prior to the introduction of iron up-gradient of the SPAR-1 & SPAR-2 test site area, air-sparging was continued for 47 days (to achieve steady-state conditions) prior to the first iron injection on November 27, 2001 (see Table 1-1). A batch injection approach was selected because transport modeling showed a strong potential for adsorption of iron on the existing soil matrix with only limited mobility of iron. As a result, a batch dose approach followed by a fresh-water slug was selected as the injection procedure to rapidly introduce and disperse iron in the groundwater system before adsorption and precipitation of iron at the injection point could occur.

The initial injection was conducted using ferric sulfate as the iron source. The injection procedure consisted of the following:

- 200 gallons of groundwater was pumped from up-gradient well STW-1 (see Figure 2-3) into a mixing tank.

- A designed 2,500 mg/L iron solution was prepared by adding 77.6 grams of sodium hydrosulfite (for oxygen reduction) and 20.76 pounds of ferric sulfate to the 200 gallons taken from STW-1. Verification sampling of the prepared iron solution was conducted and the post-preparation iron concentration was measured to be 2,460 mg/L.

- An additional 200 gallons from STW-1 was pumped into a "clean" tank, to be used as a 'freshwater flush' following introduction of the iron solution. A total of 77.6 grams of sodium hydrosulfite was added to the 200 gallons for oxygen reduction.

- The prepared iron solution was introduced into test well STW-7 by gravity feed through a ½ inch flexible line. The flexible line was inserted into the injection well to the screen zone.

- The injected iron solution was immediately followed by the 200 gallon freshwater flush into STW-7.

- A groundwater sample from down-gradient well STW-8 was collected immediately after injection was completed.

Following introduction of iron on November 27, 2001, water quality sampling at the SPAR-1 &-2 site was performed approximately daily until December 7, 2001. A second injection event was conducted on February 11, 2002 using the same general reagent solution preparation and injection procedures as the November event with the following modifications:

1. The target reagent solution was increased to approximately 3000 mg/L iron. This solution was prepared using 25 pounds of ferrous sulfate instead of ferric sulfate.

2. The 'freshwater flush' was reduced to from 200 gallons to 50 gallons.

3. Sodium hydrosulfite was not added to the 'freshwater flush' and was reduced from 77.6 grams to 40 grams for the iron solution.

These modifications allowed for more iron to be introduced into the aquifer and allowed for a higher concentration of iron to affect approximately the same amount of groundwater. Sampling was conducted daily at the SPAR-1 &-2 site between February 12th & 15th, 2002 for a total of four sampling events.

Air sparge operations and groundwater sampling were continued throughout 2002 to monitor long-term effects of iron injection and sparge operations (see Table 1-1). During this period, several additional iron injection events were conducted. These include:

- Weekly iron injection from July 17 through August 14, 2002.
- Bi-weekly (every 2 weeks) iron injection program September 5 through October 4, 2002.
- Weekly iron injection from October 17 to October 31, 2002.

Modifications to the injection schedule were made based on aquifer responses to iron injection and measured iron and arsenic concentrations in downgradient monitoring wells. This testing program allowed evaluation of the effectiveness and feasibility of iron injection to augment arsenic removal from groundwater by air sparging.

Sparging operation and monitoring for the SPAR-1 & -2 system and the SPAR-3 system continued until December 17, 2002. A final sparge sampling event was conducted January 14, 2003 to monitor response to termination of Sparge operations in December 2002.

4.3 PHASE III AIR SPARGE OPERATION RESULTS

4.3.1 Phase III Operational Parameters

As described in Section 2.3.2.1, target air injection rates for the phase III air sparge testing program were 5 to 10 cfm. Actual air injection rates and air injection pressures achieved during the Phase III program are shown in Figure 2-11.

Operating air injection rates for the SPAR-3 testing program ranged from 4 to 10 cfm but were typically within the 5 to 10 cfm target range. However, operating air injection rates for SPAR-1 and 2 were more variable and were similar to conditions observed during the Phase I testing program. Operating air injection rates ranged from 5 cfm to 16 cfm. As described in Section 2.3.2.1, the more variable operating air injection rates for the SPAR-1 and 2 testing area may be related to the more heterogeneous geology of this area as compared to the SPAR-3 area.

Water level trends associated with periods previous and during the testing program are shown in Figures 4-1, 4-5 and 4-6. Potentiometric maps for the Sparge testing area are in Appendix E. All monitored wells (including SPAR-3) showed very similar seasonal trends, with few observed discrepancies that could be attributed to effects from sparging operations. While temporary water level effects associated with the sparging operation were observed in the field, long-term trends appear to be more a reflection of seasonal declines and increases.

4.3.2 Phase III Water Quality Results:

4.3.2.1 SPAR-3 Testing Results

The sparge testing program water quality data base is in Appendix C and water quality trend plots are in Appendix F. Water quality trend plots during SPAR-3 testing are also summarized in Figures 4-2, 4-3 and 4-4.

The Phase III SPAR-3 testing program showed similar results to that observed during the limited Phase I testing program. Dissolved arsenic and iron concentrations showed a significant drop in both the SPAR-3 well and downgradient well DH-24 shortly after initiation of both Phase I and Phase III air sparging testing program. During Phase III testing, SPAR-3 arsenic concentrations dropped from 23 mg/l to a low of 0.95 mg/l. Dissolved iron concentrations declined from 10 mg/l to a low of 0.02 mg/l during the testing program. DH-24 dissolved arsenic concentrations declined from 17 mg/l to a one time low of 0.08 mg/l, but generally remained at about 1 mg/l through out the test. Similarly, dissolved iron concentrations at DH-24 declined from 9.1 mg/l to 0.027 mg/l during the test.

Concurrent with arsenic and iron concentration declines, DO concentrations increased significantly (0.03 mg/l to 9.5 mg/l) in SPAR-3 shortly after initiation of the test. DO concentrations remained elevated throughout the testing program; although a decline in DO concentrations was observed (from a high of 10.9 to a low of 4.9 mg/l) that roughly corresponded to a decline in airflow rates during the same period (see Figure 2-11). DO concentration increases (0.21 mg/l to a high of 2.75 mg/l) were also observed in down-gradient well DH-24, but to a less extent than that observed at SPAR-3. Decreases in DO concentration during the testing program resulted in correspondently minor increases in dissolved arsenic concentration.

As noted with earlier testing phases, the ratio of As^{+3}/As^{+5} at both SPAR-3 and DH-24 also decreased significantly during the Phase III testing program. This corresponded with increases in DO concentrations and resulted in decreased dissolved arsenic concentrations.

Sulfate concentrations at both SPAR-3 and DH-24 showed an increase throughout the Phase III testing program. The significance of this increase is unknown since the monitored up-gradient well (STW-1, see Appendix F) also showed an increasing sulfate trend during the testing program. Post-sparging trends for SPAR-3, DH-24, and for up-gradient well STW-1 suggest a decreasing sulfate concentration trend after sparging was completed, but the data are variable and this trend is not completely clear.

Post-Phase III testing monitoring showed a gradual return to near pre-test conditions, with gradual increases in dissolved arsenic, dissolved iron, As^{+3}/As^{+5} ratios, and corresponding decreases in DO concentrations. A total of 17 months after air sparge system shutdown (May 2004), dissolved arsenic concentrations for SPAR-3 and DH-24 were 25 and 22 mg/l, respectively, dissolved iron concentrations for SPAR-3 and DH-24 were 13.4 mg/l and 10.8 mg/l, respectively; while May 2004 DO concentrations had decreased to 0.08 mg/l and 0.014 mg/l, respectively.

4.3.2.2 SPAR-1 and SPAR-2 Phase III Testing Results

The SPAR-1 and SPAR-2 testing water quality trend plots are in Appendix F and are summarized in Figures 4-7 through 4-12. As described in Section 2.4.4 above, the Phase I Sparge testing program for using SPAR-1 and SPAR-2 showed some success in changing groundwater redox conditions and resulted in some reduction of dissolved arsenic concentrations. However, concentration decreases were not as large as decreases observed in the SPAR-3 area, where ambient dissolved iron concentrations were significantly higher, and the resulting effectiveness of arsenic removal during sparge testing was correspondingly higher. As a result, the Phase III testing program for the SPAR-1 and SPAR-2 site focused on the potential of iron injection to improve dissolved arsenic removal during air sparging.

STW-7 and STW-8

Water quality trends for iron injection well STW-7 and the next down-gradient well STW-8 are shown in Appendix F and in Figures 4-9 through 4-12. Injection well STW-7 shows significant declines in dissolved arsenic corresponding with iron injection events. As described in Table 1-1, iron was injected 11/27/01, 2/11/02, and weekly or biweekly from 7/17/02 through 10/31/02. Dissolved arsenic concentrations declined from about 30 mg/l prior to injection to a low of 0.045 mg/l when weekly or biweekly injection was conducted. Iron concentrations in the injection well ranged from lows of 0.02 mg/l between injection events to a high of 951 mg/l, but typically ranged between 100 mg/l and 800 mg/l during weekly or biweekly injection.

DO concentrations were variable and showed the effect of air sparge operation. However, DO concentrations were generally lower during weekly or biweekly iron injection events (typically 1 to 6 mg/l).

As^{+3}/As^{+5} concentration ratios in STW-7 were variable during the Phase III testing but were generally low, as expected during weekly or biweekly sampling periods. This corresponded with the lowest dissolved arsenic concentrations.

Sulfate concentrations down-gradient of iron injection well STW-7 were generally elevated, particularly in response to iron injection periods at STW-7. During weekly or biweekly injection, sulfate concentrations were typically 1000 to 3500 mg/l.

Monitoring well STW-8 is located about 30 feet down-gradient of injection well STW-7. STW-8 showed little response to the 11/27/01 and 2/11/02 iron in injection events. Dissolved arsenic concentration declines for these events were from 29 mg/l to 24 mg/l, and from 30 mg/l to 23 mg/l, respectively. Little change in arsenic concentrations were observed in STW-8 between the decline from the 2/11/02 injection event to the beginning of the weekly or biweekly injection period (7/17/02 through 10/31/02). Dissolved iron concentrations at STW-8 during the post 2/11/02 injection period remained low at about 0.02 mg/l, showing little or no evidence of iron migration to STW-8 from injection well STW-7.

However, arsenic decreases were more significant during the weekly/biweekly injection period. Dissolved arsenic concentrations declined from 23 mg/l to a low of 6.7 mg/l. The arsenic concentration low corresponded with a peak dissolved iron concentration of 13 mg/l on 8/22/02. However iron concentrations in STW-8 were typically lower after this date and generally ranged between 0.02 mg/l and 2 mg/l during the remaining iron injection period. Corresponding dissolved arsenic concentrations during this period generally ranged between 11 and 14 mg/l.

Dissolved oxygen concentrations showed effects from the sparging well with somewhat elevated DO concentrations ranging from about 3 to 5 mg/l. This compares with pre-testing DO concentrations ranging from 0.13 mg/l to 1.4 mg/l.

Arsenic As^{+3}/As^{+5} ratios were variable in STW-8 but were correspondingly lowest with lowest dissolved arsenic concentrations. Sulfate concentrations were generally elevated during the testing period ranging from a test low of about 700 mg/l to about 1300 mg/l. Concentrations of pH showed some response to the weekly/biweekly injection period with lower pH (5.5 to 6.5) values during this period.

Post testing data (see Appendix F) shows STW-8 dissolved arsenic concentrations increased somewhat, but did not attain pre-concentration results (23 mg/l). Post-testing dissolved arsenic concentrations ranged from a high of 17 mg/l in January and June 2003 to 10 mg/l in

Spring 2004. Paradoxically, dissolved iron and dissolved oxygen remain low; although the Spring 2004 did show a reduction in the As^{+3}/As^{+5} concentration ratio from measurements collected during 2003.

STW-1, STW-2, STW-3, STW-4, STW-5, STW-6, and STW-9

Water quality trends for SPAR-1 and 2 area monitoring wells are shown in Appendix F and in Figures 4-7 and 4-8. Up-gradient monitoring well STW-1 continues to show a generally declining trend in arsenic concentrations that began in fall 2000, continued through the Phase III testing period, and generally continued to decline in the post-testing period through May 2004 (see STW-1 – Appendix F). Arsenic concentrations during this period range from a high of 55 mg/l in October 2000 to a low of 17.6 mg/l in May 2004. This arsenic concentration trend roughly corresponds with a mildly increasing iron concentration trend starting November 2001 and continuing through the post-testing period through May 2004. Iron concentrations have generally increased from 0.21 mg/l in September 2001 to 0.5 mg/l in May 2004. DO concentrations have been variable with a low of 0.03 mg/l to a high of 0.89 mg/l and concluding at 0.2 mg/l during the testing period. Post-testing DO has also been variable but generally low with the most recent reading in May 2004 of 0.26 mg/l. As^{+3}/As^{+5} concentration ratios have remained high, reflecting the mobile form of arsenic at the East Helena site. Sulfate concentrations and pH have also been mildly variable during the testing and post-testing period with no obvious trends.

Monitoring wells STW-2, and STW-3, STW-4, STW-5, STW-6 and STW-9 show very similar water arsenic concentration trends to that of up-gradient monitoring well STW-1. Arsenic concentrations of most monitoring wells showed a declining trend during the testing period. Monitoring well STW-4, which has a post-testing monitoring record, also continued to show a declining trend after the test was completed.

Dissolved oxygen concentrations in monitoring wells STW-2, STW-3, STW-4, STW-5, STW-6 and STW-9 all show an increase coincident in time with the operation of the Phase III sparge testing period. With the exception of STW-4, these wells showed a rise in DO concentrations from less that 0.5 mg/l to a typical range of 5 to 10 mg/l during air sparging operation. STW-4 also showed an increasing trend after Phase III pilot test startup; however, the increase was significantly less with a high of about 1.5 mg/l. Post testing DO concentrations at STW-4 have declined with a DO concentration of 0.29 measured in May 2004.

As^{+3}/As^{+5} ratios for STW-2, and STW-3, STW-4, STW-5, STW-6 and STW-9 were typically high before the start of the test (As^{+3} typically higher than As^{+5}). The As^{+3}/As^{+5} were typically low (As^{+5} typically higher than As^{+3}) after test startup until July measurements when the ratios "flipped" and As^{+3} again became higher than As^{+5} concentrations. The reason for the increase in As^{+3} and decrease in As^{+5} is not clearly understood; however it is coincident in time with the start of the weekly/biweekly iron injection period. Monitoring wells STW-2, and STW-3, STW-4, STW-5, STW-6 and STW-9 also show a mild increase in sulfate during this period and may be showing a response to increased sulfate concentrations associated with the injection of iron during this period. Post-testing monitoring at STW-4 shows a general trend of lower sulfate concentrations since the shutdown of the pilot test program; this corresponds with a reversal of the As^{+3}/As^{+5} ratios with As^{+5} again becoming the dominant species. This also corresponds with a gradually lowering pH from about 6.47 during the test to 6.23 measured during May 2004.

5.0 SUMMARY AND RECOMMENDATIONS

In accordance with the IM Work Plan (Hydrometrics 1999), air sparging techniques were evaluated as a potential interim measure for control of arsenic migration in groundwater. Pre-testing data, collected during previous investigation efforts, suggest arsenic removal from groundwater occurs through co-precipitation/adsorption with hydrous iron oxides/hydroxides where dissolved iron is present and there is an increased oxidation state. Phase I air sparging pilot tests were conducted to evaluate if introducing oxygen to the shallow groundwater system using air sparging techniques can augment natural attenuation processes and limit off-site migration of arsenic in groundwater. This testing program showed air sparging resulted in enhanced reduction of arsenic in groundwater, but the data showed that sparging was more effective where iron was also present in groundwater. Following preparation of an interim report, (Hydrometrics 2001a), additional bench scale tests (Phase II) were conducted and the results were reported concurrent with a plan for additional Phase III air sparge testing (Hydrometrics 2001b).

The Phase III Pilot Test Program was conducted to optimize air sparging operational parameters, evaluate the effects of existing iron in groundwater on the effectiveness of air sparging for removal of arsenic, and to develop and evaluate effects of iron injection to enhance removal of arsenic by air sparging.

5.1 CONCLUSIONS

1. Introduction of oxygen through air sparging effectively raised DO concentrations.

2. The effectiveness of increasing DO in groundwater is influenced by the heterogeneous nature of the aquifer. Specifically, the presence of fine-grained silt/clay layers in the saturated zone of the generally coarse-grained aquifer can inhibit the distribution of DO during air sparging. As a result, sparge well screen designs need to provide for distribution of air across fine-grained layers. Design options include

longer screens across fine-grained layers or multiple sparge wells as were used during pilot testing.

3. Other physical changes in the aquifer that can occur as a result of air sparging are localized changes in aquifer water levels, and changes in aquifer aqueous permeability as a result of groundwater displacement by air. Pulsing injection techniques that consist of relatively short run times and relatively longer down times compensate for these effects and result in more effective distribution of dissolved oxygen in groundwater.

4. Increasing DO concentrations in groundwater resulted in geochemically oxidizing conditions, as was evident by increased concentrations of oxidized species of arsenic and iron in groundwater and decreased concentration of reduced species for these elements.

5. There was only limited evidence of increased arsenic removal rates from groundwater under oxidizing conditions where dissolved iron was absent as an initial condition (e.g. DH-50).

6. Arsenic removal rates were significantly enhanced where iron was present in groundwater. The enhanced removal where iron was present was evident during all pilot test efforts.

7. Although arsenic concentrations were successfully reduced during sparge pilot testing, the concentrations of arsenic remained above MCLs. The data suggest that removal of arsenic may have been limited by the depletion of dissolved iron in groundwater.

8. Arsenic removal in the presence of dissolved iron probably occurs through co-precipitation and enhanced adsorption and/or entrapment with other iron compounds.

Simple stoichiometric calculations compared to measured results indicate removal of arsenic in the presence of iron did not occur by co-precipitation alone.

9. The data demonstrate that enhanced reductions of arsenic concentrations by sparging are possible where the initial concentrations of dissolved iron in groundwater are higher. Where ambient iron was present, arsenic concentrations were reduced 94% to 96%, even after iron concentrations were almost totally removed from the groundwater system by air sparging.

10. Optimal removal rates where ambient iron was present was coincident with periods where higher airflow injection rates could be achieved. A one-time reduction 99.5% was observed during optimum airflow conditions. However, optimum airflow conditions are difficult to maintain due to changes in airflow associated with changing geochemical conditions, and variable performance in airflow systems. Considerable monitoring and maintenance is required for a potential increase in arsenic removal performance.

11. Where ambient iron is not present in groundwater, air sparging was significantly less effective in reducing arsenic concentrations. Although reduction in arsenic concentrations was observed, the reduction was similar in magnitude and scope to that of up-gradient and presumably unaffected monitoring sites. This up-gradient and down-gradient trend continued after the testing program and is attributed to improving groundwater quality as a result of removal of sources of arsenic in groundwater by interim measures in previous years and suspension of plant operations.

12. Injection of iron into groundwater concurrent with air sparging resulted in significant and rapid removal of arsenic in groundwater at the injection well. Arsenic reduction at the injection well location was reduced from 30 mg/l to 0.045 mg/l or 99.9 %. However, injected iron did not migrate far from the injection point and the nearest

down-gradient monitoring well 30 feet away was the only well that showed evidence of enhanced iron in groundwater samples. Where concentrations of iron in this monitoring well were highest (13 mg/l) groundwater arsenic concentrations were reduced from 23 mg/l to 6.7 mg/l or 71%. However, elevated iron concentrations in this well could not be maintained as the iron was rapidly consumed, and typical arsenic reduction was at to 43 to 52%.

13. Stratigraphy and the presence of natural iron are significant factors in the effectiveness of air sparging in reducing arsenic concentrations. Best results were obtained where there was a presence of ambient iron in groundwater, and where sediments were more homogeneous and generally finer grained (primarily sand). Generally poorer results were obtained where ambient iron in groundwater was low, and stratigraphy was more heterogeneous with the presence of sand and gravel, and interlayered clay.

14. Injected iron was rapidly removed from groundwater near the injection point by adsorption and precipitation, and attempts to enhance iron migration to down-gradient sparging areas by increasing the frequency of iron injection generally were not successful. Water quality effects at the point of injection included elevated concentrations of dissolved iron, sulfate and TDS, and reduced concentrations of arsenic, and lower pH. Only minor water quality effects were observed in down-gradient sparge test monitoring wells, which included a minor increase in sulfate concentrations; however, the frequent injection of iron induced an increase of arsenic^{+3} concentrations while arsenic^{+5} concentrations decreased. This occurred in spite of elevated DO concentrations as a result of air sparge operation.

15. Dissolved arsenic and dissolved oxygen concentrations generally returned to near pre-test concentrations after sparging operations were terminated. It is not clear if return to pre-test conditions is the result of remobilization of arsenic or simply the result of up-gradient water flow from on-plant source areas into the test area. However, the

continued long-term trend of declining arsenic in up-gradient wells and down-gradient wells suggests return to pre-test conditions is dominated by the result of continued incoming flow from on-plant source areas. Contributions of arsenic from these source areas are declining as a result of implementation of interim source control measures, on-going plant cleanup actions, and suspension of plant operations.

16. The pilot testing program demonstrated that air sparging could potentially be effective in reducing off-site arsenic migration in groundwater. However, the pilot test did not achieve MCLs, nor was it successful in significantly reducing arsenic concentrations in areas where dissolved iron is not present in groundwater. However, where ambient iron was present in groundwater, arsenic concentrations were reduced over 90%.

5.2 RECOMMENDATIONS

Air sparging can be effective in reducing arsenic concentrations in groundwater where conditions allow optimum operation and the presence of ambient iron in groundwater enhances effectiveness. However, the complexity of site stratigraphy and subsurface geochemistry makes the successful operation a complex and potentially high monitoring/maintenance effort. While sparging can result in some significant reduction of arsenic concentrations where conditions are optimum, achievement of MCLs will probably not be possible under the conditions tested at East Helena.

Sparging may be more conducive to a controlled funnel and gate approach, where the media that sparging occurs can be better controlled (emplacement of a more homogeneous sand, or sand and iron mixture for example). While this approach would probably be more effective and could potentially achieve MCLs, the expense and technical difficulty associated with emplacement of groundwater diversion/curtain walls and gate system would not make this approach appropriate as an interim measure for the site.

However, sparging, as well as other technologies under consideration, including permeable reactive barriers (PRB), water control – diversion systems, traditional pump and treat options, and other potentially applicable approaches will continue to be evaluated as part of the Corrective Measures Study (CMS) for the site and as a part of other investigation efforts. Sparging, in combination with other technologies may have applicability for long-term corrective measures at the site. Other possibilities include use of sparging at identified up-gradient source areas to change the initial oxidation state in the groundwater arsenic plume, and/or use as an air sparging in an effort to control and reduce arsenic concentrations down-gradient or off-site of the plant.

6.0 REFERENCES

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TABLES

TABLE 1-1. SUMMARY OF AIR SPARGE TESTING

Program	Date	Sampled Wells [1]	Comments	Iron Reagent Solution	Freshwater Flush
PHASE 1 Sparge System Well Construction	April and May 2000		Construct sparge wells: STW-1, STW-2, STW-3 STW-4, STW-5, STW-6, SPAR-1, SPAR-2, SPAR-3.		
Pre-Sparge Water Quality Sampling	5/10/00	STW-1, STW-2, STW-3 STW-4, STW-5, STW-6.	Collect pre-sparge baseline water quality data.		
Second Round Pre-Sparge Water Quality Sampling	5/18/00	STW-1, STW-2, STW-3 STW-4, STW-5, STW-6. DH-50	Collect pre-sparge baseline water quality data.		
Testing Sparge System	5/19/00		Evaluate sparge system air volumes and pressure readings using well SPAR-2.		
Initial Sparge System Startup (SPAR-2)	5/23/00		Start up sparge system. Set compressor to switch on and off at 15 minute intervals. Evaluate water level changes with Troll data logger at STW-5. Check dissolved oxygen at well STW-2 before startup and between sparging intervals Problems occur with air bypassing through pressure relief valve. Air injection at well SPAR-2.		
	5/24/00		Install TROLL data logger at STW-4. Check DO at STW-2 and STW-5.		
	5/25/00		Install TROLL Data logger at STW-6.		
	5/26/00		Install TROLL Data logger at STW-3.		
Initial Sparge Test Water Quality Monitoring	5/30/00	STW-1, STW-2, STW-3 STW-4, STW-5, STW-6, DH-50, SPAR-3	Collect baseline water quality data at recently installed well SPAR-3.		
	5/31/00		Move TROLL data logger to well DH-50.		
Sparge Weekly Water Quality Monitoring	6/6/00	STW-1, STW-2, STW-3 STW-4, STW-5, STW-6, DH-50			
Sparge Weekly Water Quality Monitoring	6/13/00	STW-1, STW-2, STW-3 STW-4, STW-5, STW-6, DH-50			
	6/15/02		Begin air injection at both SPAR-1 and SPAR-2.		
Sparge Weekly Water Quality Monitoring	6/21/00	STW-1, STW-2, STW-3 STW-4, STW-5, STW-6, DH-50, DH-24, EH-60			
Sparge Weekly Water Quality Monitoring	6/29/00	STW-1, STW-2, STW-3 STW-4, STW-5, STW-6, DH-50	Reset compressor timer to run on the following hourly cycle: 15 minutes on, 45 minutes off. Well caps on STW-2 and STW-3 were loose and had been blown off by air pressure.		
Sparge Bi-Weekly Water Quality Monitoring	7/13/00	STW-1, STW-2, STW-3 STW-4, STW-5, STW-6, DH-50			
Sparge Bi-Weekly Water Quality Monitoring	7/24/00	STW-1, STW-2, STW-3 STW-4, STW-5, STW-6, DH-50			

TABLE 1-1. SUMMARY OF AIR SPARGE TESTING

Program	Date	Sampled Wells [1]	Comments	Iron Reagent Solution	Freshwater Flush
Sparge Bi-Weekly Water Quality Monitoring	8/3/00	STW-1, STW-2, STW-3 STW-4, STW-5, STW-6, DH-50, EH-60, SPAR-3 DH-24			
Initial Startup of Sparge System at SPAR-3	8/9/00		Shut down air injection at SPAR-1 and SPAR-2 and begin air injection at SPAR-3.		
	8/10/00		Well cap at DH-24 off and full of water.		
Sparge Bi-Weekly Water Quality Monitoring	8/16/00	STW-1, STW-2, STW-3 STW-4, STW-5, STW-6, DH-50, EH-60, SPAR-3 DH-24			
Sparge Bi-Weekly Water Quality Monitoring	8/31/00	STW-1, STW-2, STW-3 STW-4, STW-5, STW-6, DH-50, EH-60, SPAR-3 DH-24	SPAR-3 system power supply interupted sometime between August 16th and August 31st due to power surge. SPAR-3 system restarted on August 31, 2001		
Sparge Water Quality Monitoring	9/13/00	STW-1, STW-2, STW-3 STW-4, STW-5, STW-6, DH-50, EH-60, SPAR-3 DH-24			
Sparge Water Quality Monitoring	9/22/00	EH-50, EH-60, DH-24 SPAR-3			
Sparge Water Quality Monitoring	10/3/00	STW-1, STW-2, STW-3 STW-4, STW-5, STW-6, DH-50, EH-60, SPAR-3 DH-24			
Sparge Water Quality Monitoring	10/17/00	EH-50, EH-60, DH-24 SPAR-3			
Sparge Water Quality Monitoring	11/3/00	STW-1, STW-2, STW-3 STW-4, STW-5, STW-6, DH-50, EH-60, SPAR-3 DH-24, EH-50	Sparge systems disconnected due to an electrical problem.		
	11/15/00	STW-1, STW-2, STW-3 STW-4, STW-5, STW-6, DH-50, DH-24, SPAR-3	Samples collected as part of Post RI/FS monitoring program.		
Sparge Water Quality Monitoring	12/20/00	STW-1, STW-2, STW-3 STW-4, STW-5, STW-6, DH-50, EH-60, SPAR-3 DH-24			
Sparge Water Quality Monitoring	2/7/01	STW-1, STW-4, STW-5 DH-50, EH-60, SPAR-3 DH-24, DH-16, DH-21, DH-19R, East Helena office sink			
PHASE II					
Start Bench Scale Testing	2/26/01	STW-1	Collect groundwater from STW-1 for iron bench scale testing. Assess feasibility to introduce soluble iron to the groundwater system in the air sparging area to enhance iron precipitation and arsenic removal during sparging.		
	5/14/01	STW-1, STW-2, STW-3 STW-4, STW-5, STW-6, DH-50, EH-60, SPAR-3	Samples collected as part of Post RI/FS monitoring program.		

TABLE 1-1. SUMMARY OF AIR SPARGE TESTING

Program	Date	Sampled Wells [1]	Comments	Iron Reagent Solution	Freshwater Flush
		DH-24			
Conduct Column Leach Tests	6/15/01		Assess the solubility of various iron reagents in groundwater from the site. Evaluate iron attentuation by site soils. Evaluate the effect of varying iron concentrations on groundwater pH. Evaluate the effect of iron concentrations and pH on iron/arsenic removal rates. Evaluate time required for iron/arsenic precipitation. Evaluate the stability of arsenic-bearing precipitates.		
PHASE III					
Sparge Well Construction	7/17/01		Drill and complete additional sparge wells STW-7, STW-8, and STW-9 (7/17/01 - 7/19/01).		
	8/10/01	STW-7, STW-8, STW-9			
Pre-Start Up Sparge Water Quality Monitoring	9/26/01	STW-1, STW-2, STW-3 STW-4, STW-5, STW-6, STW-7, STW-8, STW-9 DH-50, DH-24, SPAR-3			
Start up SPAR-1 and SPAR-2 Air Compressor	10/11/01		Air compressors wired properly by electrician. Air compressor turned on for SPAR-1 & 2 site. Compressor for SPAR-3 still not working. Set SPAR-1 & 2 compressor to run for 15 minutes every other hour on odd numbered hours. (I.e.; 1,3,5) Air injection at wells SPAR-1 and SPAR-2.		
	10/19/01	STW-2, STW-3, STW-4 STW-5, STW-6, STW-7 STW-8, STW-9, DH-50 DH-24, SPAR-3	Water quality monitoring included only collection of field parameters and iron speciation. No laboratory samples. SPAR-3 system waiting on new compressor switch.		
	11/2/01	STW-1, STW-2, STW-3 STW-4, STW-5, STW-6, STW-7, STW-8, STW-9 DH-50, DH-24, SPAR-3	Water quality monitoring included only collection of field parameters and iron speciation. No laboratory samples.		
Re-start SPAR-3 sparge system	11/6/01		Turned on SPAR-3 air sparge system. Set system to run for 15 minutes every other hour on even numbered hours (I.e.; 2, 4)		
	11/8/01	DH-24, DH-50	Samples collected as part of Post RI/FS monitoring program.		
	11/20/01	STW-1, STW-2, STW-3 STW-4, STW-5, STW-6, STW-7, STW-8, STW-9 DH-50, DH-24, SPAR-3			
Initial Iron Injection at SPAR-1 & 2	11/27/01			200 gallons groundwater obtained from STW-1 2500 mg/L iron solution created by mixing 77.6 grams of sodium hydrosulfite and 20.76 pounds of ferric sulfate with 200 gallons of groundwater	200 gallons groundwater obtained from STW-1 Added 77.6 grams of sodium hydrosulfite to the 200 gallons of groundwater
	11/28/01	STW-7, STW-8	Samples analyzed for dissolved iron and sulfate in the field.		
	11/30/01	STW-2, STW-3, STW-7, STW-8, STW-9			
	12/3/01	STW-7, STW-8	Collected samples for field parameters. Iron and sulfate analyzed in the field.		
	12/4/01	STW-2, STW-3, STW-7, STW-8, STW-9			
	12/7/01	STW-1, STW-2, STW-3- STW-4, STW-5, STW-6, STW-7, STW-8, STW-9	SPAR -3 well cap not tight.		

TABLE 1-1. SUMMARY OF AIR SPARGE TESTING

Program	Date	Sampled Wells [1]	Comments	Iron Reagent Solution	Freshwater Flush
		DH-50, DH-24, SPAR-3			
	12/12/01	STW-1, STW-2, STW-3 STW-4, STW-5, STW-6, STW-7, STW-8, STW-9	Samples analyzed for field parameters, iron, and sulfate.		
	12/14/01	STW-2, STW-3, STW-4 STW-5, STW-6, STW-7 STW-8, STW-9, DH-50			
	12/19/01	STW-1, STW-2, STW-3 STW-4, STW-5, STW-6, STW-7, STW-8, STW-9 DH-50, DH-24, SPAR-3			
	12/27/01	STW-2, STW-3, STW-4 STW-5, STW-6, STW-7 STW-8, DH-50			
	1/10/02	STW-1, STW-2, STW-3 STW-4, STW-5, STW-6, STW-7, STW-8, STW-9 DH-50, DH-24, SPAR-3			
	1/16/02	STW-2, STW-3, STW-4 STW-5, STW-6, STW-7 STW-8, STW-9, DH-50			
	1/23/02	STW-1, STW-2, STW-3 STW-4, STW-5, STW-6, STW-7, STW-8, STW-9 DH-50, DH-24, SPAR-3			
	2/5/02	STW-1, STW-2, STW-3 STW-4, STW-5, STW-6, STW-7, STW-8, STW-9 DH-50, DH-24, SPAR-3			
Second Iron Injection at SPAR-1 & 2	2/11/02	STW-2, STW-3, STW-7 STW-8, STW-9	Injected 3000 ppm ferrous sulfate solution into STW-7.	200 gallons groundwater obtained from STW-1 3000 mg/L iron solution created by mixing 40 grams of sodium hydrosulfite and 25 pounds of ferrous sulfate with 200 gallons of groundwater	50 gallons of groundwater obtained from STW-1
	2/12/02	STW-2, STW-3, STW-7 STW-8, STW-9	Sampled for field parameters and total iron.		
	2/13/02	STW-2, STW-3, STW-7 STW-8, STW-9, EH-100			
	2/14/02	STW-2, STW-3, STW-7 STW-8, STW-9			
	2/15/02	STW-2, STW-3, STW-7 STW-8, STW-9			
	2/19/02	STW-1, STW-2, STW-3 STW-4, STW-5, STW-6, STW-7, STW-8, STW-9 DH-50, DH-24, SPAR-3			
	2/22/02	STW-2, STW-3, STW-5 STW-7, STW-8, STW-9			
	2/26/02	EH-100	Collected water quality samples from top and bottom of screen.		
	2/27/02	STW-1, STW-2, STW-3 STW-4, STW-5, STW-6, STW-7, STW-8, STW-9			

TABLE 1-1. SUMMARY OF AIR SPARGE TESTING

Program	Date	Sampled Wells [1]	Comments	Iron Reagent Solution	Freshwater Flush
		DH-50			
	3/6/02	STW-1, STW-2, STW-3 STW-4, STW-5, STW-6, STW-7, STW-8, STW-9 DH-50, DH-24, SPAR-3	Data not inadvertently not included in data base.		
	3/19/02	STW-1,STW-9, DH-24, SPAR-3	Data not inadvertently not included in data base.		
	3/26/02	STW-1, STW-2, STW-3 STW-4, STW-5, STW-6, STW-7, STW-8, STW-9 DH-50, DH-24, SPAR-3	Data not inadvertently not included in data base.		
	4/19/02	STW-1, STW-2, STW-3 STW-4, STW-5, STW-6, STW-7, STW-8, STW-9 DH-24, SPAR-3, DH-50			
	5/10/02	STW-4, STW-5, STW-6, STW-7, STW-8, STW-9 DH-24, SPAR-3			
	5/30/02	DH-24, DH-50	Samples collected as part of Post RI/FS monitoring program.		
	6/6/02	STW-1, STW-2, STW-3 STW-4, STW-5, STW-6, STW-7, STW-8, STW-9 DH-24, SPAR-3			
Weekly injection program Initiated. Third iron injection at SPAR-1 & 2 Sparge System	7/17/02	*Pre-Injection Sampling* STW-2, STW-3, STW-4 STW-7, STW-8	*Sampled wells prior to iron injection at STW-7.*	*200 gallons groundwater obtained from STW-1* 3000 mg/L iron solution created by mixing 40 grams of sodium hydrosulfite and 25 pounds of ferrous sulfate with 200 gallons of groundwater	*50 gallons of groundwater obtained from STW-1*
	7/19/02	Post-Injection Sampling STW-7, STW-8			
Fourth iron injection at SPAR-1 & 2 Sparge System	7/24/02	Pre-Injection Sampling STW-2, STW-3, STW-4 STW-7, STW-8	Sampled wells prior to iron injection at STW-7.	200 gallons groundwater obtained from DH-51 3000 mg/L iron solution created by mixing 40 grams of sodium hydrosulfite and 25 pounds of ferrous sulfate with 200 gallons of groundwater	50 gallons of groundwater obtained from DH-51
	7/25/02	Post-Injection Sampling STW-7, STW-8			
Fifth iron injection at SPAR-1 & 2 Sparge System	7/31/02	Pre-Injection Sampling STW-2, STW-3, STW-4 STW-7, STW-8	Sampled wells prior to iron injection at STW-7.	200 gallons groundwater obtained from DH-51 3000 mg/L iron solution created by mixing 40 grams of sodium hydrosulfite and 25 pounds of ferrous sulfate with 200 gallons of groundwater	50 gallons of groundwater obtained from DH-51
	8/1/02	Post-Injection Sampling STW-7, STW-8			
Sixth iron injection at SPAR-1 & 2 Sparge System	8/8/02	Pre-Injection Sampling STW-1, STW-2, STW-3 STW-4, STW-5, STW-6, STW-7, STW-8, STW-9, DH-50 Also Sampled SPAR-3 System DH-24, SPAR-3	Sampled wells prior to iron injection at STW-7.	200 gallons groundwater obtained from DH-51 3000 mg/L iron solution created by mixing 40 grams of sodium hydrosulfite and 25 pounds of ferrous sulfate with 200 gallons of groundwater	50 gallons of groundwater obtained from DH-51
	8/9/02	Post-Injection Sampling STW-7, STW-8			
Seventh iron injection at SPAR-1 & 2 Sparge System	8/14/02	Pre-Injection Sampling STW-2, STW-3, STW-4 STW-7, STW-8	Sampled wells prior to iron injection at STW-7.	200 gallons groundwater obtained from DH-51 3000 mg/L iron solution created by mixing 40 grams of sodium hydrosulfite and 25 pounds of ferrous	50 gallons of groundwater obtained from DH-51

TABLE 1-1. SUMMARY OF AIR SPARGE TESTING

Program	Date	Sampled Wells [1]	Comments	Iron Reagent Solution	Freshwater Flush
				sulfate with 200 gallons of groundwater	
	8/15/02	Post-Injection Sampling STW-7, STW-8			
	8/20/02		EPA constructs new PRB wells. Instruments DH-24, DH-50 and STW-1. Removed expansion caps so venting to atmosphere during the period August 20 through September 30, 2002.		
	8/22/02	STW-2, STW-3, STW-4 STW-7, STW-8			
	8/28/02	STW-2, STW-3, STW-4 STW-7, STW-8			
Eighth iron injection at SPAR-1 & 2 Sparge System	9/5/02	Pre-Injection Sampling STW-2, STW-3, STW-4 STW-7, STW-8	Sampled wells prior to iron injection at STW-7.	200 gallons groundwater obtained from DH-51 3000 mg/L iron solution created by mixing 40 grams of sodium hydrosulfite and 25 pounds of ferrous sulfate with 200 gallons of groundwater	50 gallons of groundwater obtained from DH-51
	9/6/02	Post-Injection Sampling STW-7, STW-8			
	9/12/02	STW-7, STW-8, DH-24			
Nineth iron injection at SPAR-1 & 2 Sparge System	9/19/02	Pre-Injection Sampling STW-2, STW-3, STW-4 STW-7, STW-8	Sampled wells prior to iron injection at STW-7.	200 gallons groundwater obtained from DH-51 3000 mg/L iron solution created by mixing 40 grams of sodium hydrosulfite and 25 pounds of ferrous sulfate with 200 gallons of groundwater	50 gallons of groundwater obtained from DH-51
	9/20/02	Post-Injection Sampling STW-7, STW-8			
	9/26/02	STW-1, STW-2, STW-3 STW-4, STW-5, STW-6, STW-7, STW-8, STW-9 DH-50, DH-24, SPAR-3			
Tenth iron injection at SPAR-1 & 2 Sparge System	10/4/02	Pre-Injection Sampling STW-2, STW-3, STW-4 STW-7, STW-8	Sampled wells prior to iron injection at STW-7.	200 gallons groundwater obtained from DH-51 3000 mg/L iron solution created by mixing 40 grams of sodium hydrosulfite and 25 pounds of ferrous sulfate with 200 gallons of groundwater	50 gallons of groundwater obtained from DH-51
	10/5/02	Post-Injection Sampling STW-7, STW-8			
Eleventh iron injection at SPAR-1 & 2 Sparge System	10/17/02	STW-2, STW-3, STW-4 STW-7, STW-8	Sampled wells prior to iron injection at STW-7. Frozen well cap at STW-8.	200 gallons groundwater obtained from DH-51 3000 mg/L iron solution created by mixing 40 grams of sodium hydrosulfite and 25 pounds of ferrous sulfate with 200 gallons of groundwater	50 gallons of groundwater obtained from DH-51
Twelfth iron injection at SPAR-1 & 2 Sparge System	10/23/02	STW-2, STW-3, STW-4 STW-7, STW-8	Sampled wells prior to iron injection at STW-7.	200 gallons groundwater obtained from DH-51 3000 mg/L iron solution created by mixing 40 grams of sodium hydrosulfite and 25 pounds of ferrous sulfate with 200 gallons of groundwater	50 gallons of groundwater obtained from DH-51
Thirteenth iron injection at SPAR-1 & 2 Sparge System	10/31/02	STW-2, STW-3, STW-4 STW-7, STW-8	Sampled wells prior to iron injection at STW-7.	200 gallons groundwater obtained from DH-51 3000 mg/L iron solution created by mixing 40 grams of sodium hydrosulfite and 25 pounds of ferrous sulfate with 200 gallons of groundwater	50 gallons of groundwater obtained from DH-51
	11/13/02	STW-1, STW-2, STW-3 STW-4, STW-5, STW-6, STW-7, STW-8, STW-9 DH-50, DH-24, SPAR-3	Samples collected as part of Post RI/FS monitoring program.		

TABLE 1-1. SUMMARY OF AIR SPARGE TESTING

Program	Date	Sampled Wells [1]	Comments	Iron Reagent Solution	Freshwater Flush
Shutdown Sparge Systems	12/17/02	STW-7, STW-8, SPAR-3 DH-24	Turn off sparge systems		
Post Sparge Sampling	1/14/03	STW-7, STW-8, DH-24			

Notes: (1) Wells were generally sampled for field parameters (static water level,pH, specific conductance, dissolved oxygen, and temperature) common ions (sulfate, alkalinity), dissolved arsenic and iron, and arsenic speciation (As+3/As+5). Additional field parameters (Eh and Fe+2/Fe+3) and a more extensive suite of parameters for common ions and dissolved metals were analyzed for samples collected during 2000 and 2001.

TABLE 2-1. CONSTRUCTION OF SPARGING WELLS AND MONITORING WELLS INSTALLED DURING INTERIM MEASURES SPARGING PILOT TEST

Well Name	Date Installed	Phase	Casing Size (inches)	Ground Surface Elevation (feet)	Measuring Point (MP) Elevation (feet)	Static Water Level (feet below MP)	Static Water Elevation (feet)	Total Depth (feet)	Screen Interval (ft bgs)
Sparging Wells									
SPAR-1	4/27/00	I	2	3898.72	3901.14	33	3868.14	40	38-40
SPAR-2	4/28/00	I	2	3898.44	3901.62	33	3868.62	41	36-39
SPAR-3	5/22/00	I	2	3898.04	3900.59	32.86	3867.73	40	35-37
Monitoring Wells									
STW-1	4/26/00	I	2	3899.77	3902.21	32.24	3869.97	40	33-38
STW-2	4/25/00	I	2	3898.30	3900.89	31.47	3869.42	40	34-39
STW-3	4/29/00	I	2	3898.73	3901.39	31.87	3869.52	40	34.5-39.5
STW-4	5/2/00	I	2	3898.09	3900.59	31.18	3869.41	40	32-37
STW-5	5/1/00	I	2	3897.74	3900.45	31.06	3869.39	40	34-39
STW-6	4/30/00	I	2	3898.11	3900.76	31.31	3869.45	40	34-39
STW-7	7/17/01	III	2	3899.828	3902.118	32.43	3869.69	40	25-40
STW-8	7/18/01	III	2	3899.534	3902.034	32.42	3869.61	40	35-40
STW-9	7/19/01	III	2	3898.399	3900.65	31.23	3869.42	40	35-40

TABLE 2-2. SPARGING TEST GROUNDWATER SAMPLE COLLECTION AND ANALYSIS

Sample Location[1]	Purpose	Sample Dates	Analytical Suite[2,3,4]
PHASE 1 STW-1, STW-2, STW-3 STW-4, STW-5, STW-6 DH-50 (E)	Phase I Pretest Monitoring Characterize groundwater chemistry prior to air sparging	04/25/2000-05/10/2000	F,C,M, A
STW-1, STW-2, STW-3 STW-4, STW-5, STW-6 DH-50 (E)	Second Round Pretest Monitoring Characterize groundwater chemistry prior to air sparging	5/18/00	F,M
STW-1, STW-2, STW-3 STW-4, STW-5, STW-6 DH-50 (E)	First Round Sparge Test Monitoring Characterize groundwater chemistry during Phase I air sparging test	5/30/00	F,M
STW-1, STW-2, STW-3 STW-4, STW-5, STW-6 DH-50 (E)	Second Round Sparge Test Monitoring Characterize groundwater chemistry duringPhase II air sparging test	6/6/00	F,M,A
STW-1, STW-2, STW-3 STW-4, STW-5, STW-6 DH-50 (E)	Third Round Sparge Test Monitoring Characterize groundwater chemistry during Phase I air sparging test	6/13/00	F,M
STW-1, STW-2, STW-3 STW-4, STW-5, STW-6 DH-50 (E), DH-24 (E), DH-51 (E) EH-60 (E)	Fourth Round Sparge Test Monitoring Characterize groundwater chemistry during Phase I air sparging test	6/21/00	F,C,M, A
STW-1, STW-2, STW-3 STW-4, STW-5, STW-6 DH-50 (E)	Fifth Through Eighth Round Sparge Test Monitoring Characterize groundwater chemistry during Phase I air sparging test	6/29/00 7/13/00 7/24/00	F,C,M,A
STW-1, STW-2, STW-3 STW-4, STW-5, STW-6 DH-50 (E), DH-24 (E), EH-60 (E) SPAR-3	Final Rounds Sparge Test Monitoring Characterize groundwater chemistry during Phase I air sparging test	8/3/00 8/16/00	F,A, As(diss)
STW-1, STW-2, STW-3 STW-4, STW-5, STW-6 DH-50 (E), DH-24 (E), EH-60 (E) SPAR-3	First Four Rounds Sparge Test Monitoring Characterize groundwater chemistry during second Phase I air sparging test	8/16/00 8/31/00 9/13/00	F,A, As(diss)
SPAR-3, DH-24 (E), EH-60 (E) EH-50 (E)	Fifth Round Sparge Test Monitoring Characterize groundwater chemistry during second Phase I air sparging test	10/17/00	F,A, As(diss)
STW-1, STW-4, DH-50 (E) DH-24 (E), SPAR-3, EH-60 (E) EH-50 (E)	Sixth Round Sparge Test Monitoring Characterize groundwater chemistry during second Phae I air sparging test	11/3/00	F,A, As(diss)
PHASE 3 STW-1, STW-2, STW-3 STW-4, STW-5, STW-6 DH-50 (E), DH-24 (E), EH-60 (E) SPAR-3	Seventh Round Sparge Test Monitoring Characterize groundwater chemistry during second Phae I air sparging test	12/20/00	F,C,M,A

TABLE 2-2. SPARGING TEST GROUNDWATER SAMPLE COLLECTION AND ANALYSIS

Sample Location[1]	Purpose	Sample Dates	Analytical Suite[2,3,4]
STW-1, STW-4, STW-5 DH-50, EH-60, SPAR-3 DH-24, DH-16, DH-21, DH-19R, East Helena office sink	Eighth Round Sparge Test Monitoring Characterize groundwater chemistry during second Phase I air sparging test	2/7/01	F,A,As(diss), Fe (diss)
STW-7, STW-8, STW-9	Baseline monitoring of SPAR-1 & 2 sparge system wells	8/10/01	F,C,M, A
STW-1, STW-2, STW-3 STW-4, STW-5, STW-6, STW-7, STW-8, STW-9 DH-50, DH-24, SPAR-3	Pre-Start Up Sparge Water Quality Monitoring	9/26/01	F,C,M,A
STW-2, STW-3, STW-4 STW-5, STW-6, STW-7 STW-8, STW-9, DH-50 DH-24, SPAR-3	First Round Sparge Test Monitoring Characterize groundwater chemistry during Phase III air sparging test	10/19/01	F,Fe Spec
STW-1, STW-2, STW-3 STW-4, STW-5, STW-6, STW-7, STW-8, STW-9 DH-50, DH-24, SPAR-3	Second Round Sparge Test Monitoring Characterize groundwater chemistry during Phase III air sparging test	11/2/01	F,Fe Spec
STW-1, STW-2, STW-3 STW-4, STW-5, STW-6, STW-7, STW-8, STW-9 DH-50, DH-24, SPAR-3	Third Round Sparge Test Monitoring Characterize groundwater chemistry during Phase III air sparging test	11/20/01	F,C,M,A
STW-7, STW-8	Post injection sampling after initial iron injection at SPAR-1 & 2 Characterize groundwater chemistry during iron injection at SPAR-1 & 2	11/28/01	Fe, SO4
STW-2, STW-3, STW-7, STW-8, STW-9	Characterize groundwater chemistry after initial iron injection at SPAR-1 & 2	11/30/01	F, As (diss), Fe spec
STW-7, STW-8	Characterize groundwater chemistry after initial iron injection at SPAR-1 & 2	12/3/01	F, Fe, SO4
STW-2, STW-3, STW-7, STW-8, STW-9	Characterize groundwater chemistry after initial iron injection at SPAR-1 & 2	12/4/01	F,C, As (diss), Fe spec
STW-1, STW-2, STW-3 STW-4, STW-5, STW-6, STW-7, STW-8, STW-9 DH-50, DH-24, SPAR-3	Characterize groundwater chemistry after initial iron injection at SPAR-1 & 2	12/7/01	F,CM,A
STW-1, STW-2, STW-3 STW-4, STW-5, STW-6, STW-7, STW-8, STW-9	Characterize groundwater chemistry after initial iron injection at SPAR-1 & 2	12/12/01	F, Fe, SO4

TABLE 2-2. SPARGING TEST GROUNDWATER SAMPLE COLLECTION AND ANALYSIS

Sample Location[1]	Purpose	Sample Dates	Analytical Suite[2,3,4]
STW-2, STW-3, STW-4 STW-5, STW-6, STW-7 STW-8, STW-9, DH-50	Characterize groundwater chemistry after initial iron injection at SPAR-1 & 2	12/14/01	F,C, As (diss), Fe spec
STW-1, STW-2, STW-3 STW-4, STW-5, STW-6, STW-7, STW-8, STW-9 DH-50, DH-24, SPAR-3	Characterize groundwater chemistry after initial iron injection at SPAR-1 & 2	12/19/01	F,CM,A
STW-2, STW-3, STW-4 STW-5, STW-6, STW-7 STW-8, DH-50	Characterize groundwater chemistry after initial iron injection at SPAR-1 & 2	12/27/01	F,C,As (diss), Fe (diss)
STW-1, STW-2, STW-3 STW-4, STW-5, STW-6, STW-7, STW-8, STW-9 DH-50, DH-24, SPAR-3	Characterize groundwater chemistry after initial iron injection at SPAR-1 & 2	1/10/02	F,CM,A
STW-2, STW-3, STW-4 STW-5, STW-6, STW-7 STW-8, STW-9, DH-50	Characterize groundwater chemistry after initial iron injection at SPAR-1 & 2	1/16/02	F,C,As (diss), Fe (diss)
STW-1, STW-2, STW-3 STW-4, STW-5, STW-6, STW-7, STW-8, STW-9 DH-50, DH-24, SPAR-3	Characterize groundwater chemistry after initial iron injection at SPAR-1 & 2	1/23/02	F,CM,A
STW-1, STW-2, STW-3 STW-4, STW-5, STW-6, STW-7, STW-8, STW-9 DH-50, DH-24, SPAR-3	Characterize groundwater chemistry after initial iron injection at SPAR-1 & 2	2/5/02	F,CM,A
STW-2, STW-3, STW-7 STW-8, STW-9	Characterize groundwater chemistry prior to second iron injection at SPAR-1 & 2	2/11/02	F,C,As (diss), Fe (diss)
STW-2, STW-3, STW-7 STW-8, STW-9	Characterize groundwater chemistry prior to second iron injection at SPAR-1 & 2	2/12/02	F,C,As (diss), Fe (diss)
STW-2, STW-3, STW-7 STW-8, STW-9, EH-100	Characterize groundwater chemistry prior to second iron injection at SPAR-1 & 2	2/13/02	F,C,As (diss), Fe (diss)
STW-2, STW-3, STW-7 STW-8, STW-9	Characterize groundwater chemistry prior to second iron injection at SPAR-1 & 2	2/14/02	F,C,As (diss), Fe (diss)
STW-2, STW-3, STW-7 STW-8, STW-9	Characterize groundwater chemistry prior to second iron injection at SPAR-1 & 2	2/15/02	F,C,As (diss), Fe (diss)
STW-1, STW-2, STW-3 STW-4, STW-5, STW-6, STW-7, STW-8, STW-9 DH-50, DH-24, SPAR-3	Characterize groundwater chemistry prior to second iron injection at SPAR-1 & 2	2/19/02	F,CM,A
STW-2, STW-3, STW-5 STW-7, STW-8, STW-9	Characterize groundwater chemistry prior to second iron injection at SPAR-1 & 2	2/22/02	F,C,As (diss), Fe (diss)
STW-1, STW-2, STW-3 STW-4, STW-5, STW-6, STW-7, STW-8, STW-9 DH-50	Characterize groundwater chemistry prior to second iron injection at SPAR-1 & 2	2/27/02	F,C,As (diss), Fe (diss)

TABLE 2-2. SPARGING TEST GROUNDWATER SAMPLE COLLECTION AND ANALYSIS

Sample Location[1]	Purpose	Sample Dates	Analytical Suite[2,3,4]
STW-1, STW-2, STW-3 STW-4, STW-5, STW-6, STW-7, STW-8, STW-9 DH-50, DH-24, SPAR-3	Characterize groundwater chemistry prior to second iron injection at SPAR-1 & 2	3/6/02	F,C,As (diss), Fe (diss)
STW-1,STW-9, DH-24, SPAR-3	Characterize groundwater chemistry prior to second iron injection at SPAR-1 & 2	3/19/02	F,C,As (diss), Fe (diss)
STW-1, STW-2, STW-3 STW-4, STW-5, STW-6, STW-7, STW-8, STW-9 DH-50, DH-24, SPAR-3	Characterize groundwater chemistry prior to second iron injection at SPAR-1 & 2	3/26/02	F,C,As (diss), Fe (diss)
STW-1, STW-2, STW-3 STW-4, STW-5, STW-6, STW-7, STW-8, STW-9 DH-24, SPAR-3, DH-50	Characterize groundwater chemistry prior to second iron injection at SPAR-1 & 2	4/19/02	F,C,M,A
STW-4, STW-5, STW-6, STW-7, STW-8, STW-9 DH-24, SPAR-3	Characterize groundwater chemistry prior to second iron injection at SPAR-1 & 2	5/10/02	F,C,M,A
STW-1, STW-2, STW-3 STW-4, STW-5, STW-6, STW-7, STW-8, STW-9 DH-24, SPAR-3	Characterize groundwater chemistry prior to second iron injection at SPAR-1 & 2	6/6/02	F,C,M,A
STW-2, STW-3, STW-4 STW-7, STW-8	Characterize groundwater chemistry prior to third iron injection at SPAR-1 & 2	7/17/02	F,C,As (diss), Fe (diss)
STW-7, STW-8	Characterize groundwater chemistry after third iron injection at SPAR-1 & 2	7/19/02	F,C,As (diss), Fe (diss)
STW-2, STW-3, STW-4 STW-7, STW-8	Characterize groundwater chemistry prior to fourth iron injection at SPAR-1 & 2	7/24/02	F,C,M,A
STW-7, STW-8	Characterize groundwater chemistry after fourth iron injection at SPAR-1 & 2	7/25/02	F,C,M,A
STW-2, STW-3, STW-4 STW-7, STW-8	Characterize groundwater chemistry prior to fifth iron injection at SPAR-1 & 2	7/31/02	F,C,A,As(diss), Fe (Diss)
STW-7, STW-8	Characterize groundwater chemistry after fifth iron injection at SPAR-1 & 2	8/1/02	F,C,A,As(diss), Fe (Diss)
STW-1, STW-2, STW-3 STW-4, STW-5, STW-6, STW-7, STW-8, STW-9, DH-50 DH-24, SPAR-3	Characterize groundwater chemistry prior to sixth iron injection at SPAR-1 & 2	8/8/02	F,C,A,As(diss), Fe (Diss)
STW-7, STW-8	Characterize groundwater chemistry after sixth iron injection at SPAR-1 & 2	8/9/02	F,C,A,As(diss), Fe (Diss)
STW-2, STW-3, STW-4 STW-7, STW-8	Characterize groundwater chemistry prior to seventh iron injection at SPAR-1 & 2	8/14/02	F,C,A,As(diss), Fe (Diss)

TABLE 2-2. SPARGING TEST GROUNDWATER SAMPLE COLLECTION AND ANALYSIS

Sample Location[1]	Purpose	Sample Dates	Analytical Suite[2,3,4]
STW-7, STW-8	Characterize groundwater chemistry after seventh iron injection at SPAR-1 & 2	8/15/02	F,C,A,As(diss), Fe (Diss)
STW-2, STW-3, STW-4 STW-7, STW-8	Characterize groundwater chemistry after seventh iron injection at SPAR-1 & 2	8/22/02	F,C,A,As(diss), Fe (Diss)
STW-2, STW-3, STW-4 STW-7, STW-8	Characterize groundwater chemistry after seventh iron injection at SPAR-1 & 2	8/28/02	F,C,A,As(diss), Fe (Diss)
STW-2, STW-3, STW-4 STW-7, STW-8	Characterize groundwater chemistry prior to eighth iron injection at SPAR-1 & 2	9/5/02	F,C,A,As(diss), Fe (Diss)
STW-7, STW-8	Characterize groundwater chemistry after eighth iron injection at SPAR-1 & 2	9/6/02	F,C,A,As(diss), Fe (Diss)
STW-7, STW-8, DH-24	Characterize groundwater chemistry after eighth iron injection at SPAR-1 & 2	9/12/02	F,C,A,As(diss), Fe (Diss)
STW-2, STW-3, STW-4 STW-7, STW-8	Characterize groundwater chemistry prior to ninth iron injection at SPAR-1 & 2	9/19/02	F,C,A,As(diss), Fe (Diss)
STW-7, STW-8	Characterize groundwater chemistry after ninth iron injection at SPAR-1 & 2	9/20/02	F,C,A,As(diss), Fe (Diss)
STW-1, STW-2, STW-3 STW-4, STW-5, STW-6, STW-7, STW-8, STW-9 DH-50, DH-24, SPAR-3	Characterize groundwater chemistry after ninth iron injection at SPAR-1 & 2	9/26/02	F,C,A,As(diss), Fe (Diss)
STW-2, STW-3, STW-4 STW-7, STW-8	Characterize groundwater chemistry prior to tenth iron injection at SPAR-1 & 2	10/4/02	F,C,A,As(diss), Fe (Diss)
STW-7, STW-8	Characterize groundwater chemistry after tenth iron injection at SPAR-1 & 2	10/5/02	F,C,A,As(diss), Fe (Diss)
STW-2, STW-3, STW-4 STW-7, STW-8	Characterize groundwater chemistry prior to eleventh iron injection at SPAR-1 & 2	10/17/02	F,C,A,As(diss), Fe (Diss)
STW-2, STW-3, STW-4 STW-7, STW-8	Characterize groundwater chemistry prior to twelfth iron injection at SPAR-1 & 2	10/23/02	F,C,A,As(diss), Fe (Diss)
STW-2, STW-3, STW-4 STW-7, STW-8	Characterize groundwater chemistry prior to thirteenth iron injection at SPAR-1 & 2	10/31/02	F,C,A,As(diss), Fe (Diss)
STW-1, STW-2, STW-3 STW-4, STW-5, STW-6, STW-7, STW-8, STW-9 DH-50, DH-24, SPAR-3	Characterize groundwater chemistry as part of Post RI/FS Monitoring Program	11/13/02	F,C,M,A
STW-7, STW-8, SPAR-3 DH-24	Characterize groundwater chemistry prior to sparge system shutdown	12/17/02	F,C,A,As(diss), Fe (Diss)

TABLE 2-2. SPARGING TEST GROUNDWATER SAMPLE COLLECTION AND ANALYSIS

Sample Location(1)	Purpose	Sample Dates	Analytical Suite(2,3,4)
STW-7, STW-8, DH-24	Characterize groundwater chemistry after sparge system shutdown	1/14/03	F,C,A,As(diss), Fe (Diss)

(1) (E) = Existing wells

(2) F = field parameters C= common ions M = metals A= arsenic speciation, As(diss) = dissolved arsenic Fe (diss) = dissolved iron, Fe spec = iron speciation SO4= sulfate

(3) Samples were analyzed for dissolved constituents (field-filtered through a 0.45 μm filter).

(4) Methods from EPA's *Test Methods for Evaluating Solid Waste, SW-846* (1992) or *Methods for Chemical Analysis of Water and Wastes* (1983).
For trace constituents and major cations, Method 6010 is ICP, Method 6020 is ICP-MS, and other methods are flame or graphite furnace AA.

TABLE 2-3. PARAMETER LIST

Analytical Parameters	Laboratory Methods[4]	Project Detection Limit Goal (mg/L)
Field Parameters (F)		
pH	N/A	N/A
specific conductance		
dissolved oxygen		
temperature		
Eh		
Fe+2/Fe+3		
SWL (static water level)		
Laboratory Parameters Common Constituents (C)		
pH	150.1	
SC	120.1	
Ca	6010A/7140	5
Mg	6010A/7450	5
Na	6010A/7770	5
K	6010A/7610	5
HCO_3	310.1	1
CO3	310.1	1
SO_4	9036	1
Cl	325.2	1
Trace Constituents[3] (M)		
As (diss)	7060/6010A/6020	0.005
Cd (diss)	7131/7130/6010A/6020	0.001
Fe (diss)	6010A	0.02
Mn (diss)	6010A	0.015
Pb (diss)	7421/7420/6010A/6020	0.005
Zn (diss)	7950/6010A/6020	0.02
Arsenic Speciation (A)		
As3+	7060/6010A/6020	0.005
As5+	7060/6010A/6020	0.005

(1) (E) = Existing wells

(2) F = field parameters C = common ions M = metals A= arsenic speciation

(3) Samples were analyzed for dissolved constituents (field-filtered through a 0.45 μm filter).

(4) Methods from EPA's *Test Methods for Evaluating Solid Waste, SW-846* (1992) or *Methods for Chemical Analysis of Water and Wastes* (1983). For trace constituents and major cations, Method 6010 is ICP, Method 6020 is ICP-MS, and other methods are flame or graphite furnace AA.

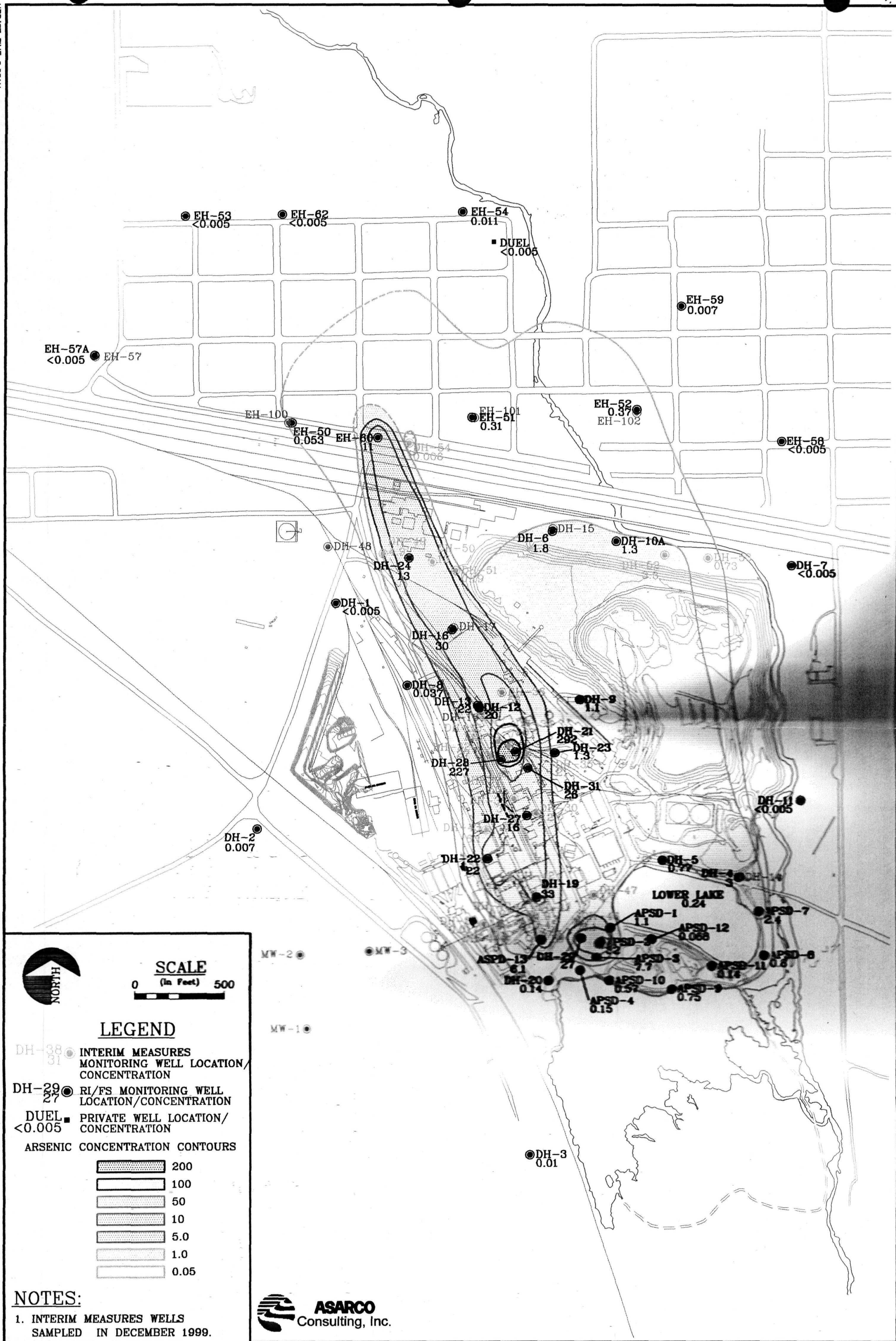
(5) Field duplicates and blanks were collected at a minimum frequency of 1 per 20 field samples.

TABLE 2-4 BASELINE WATER QUALITY RESULTS

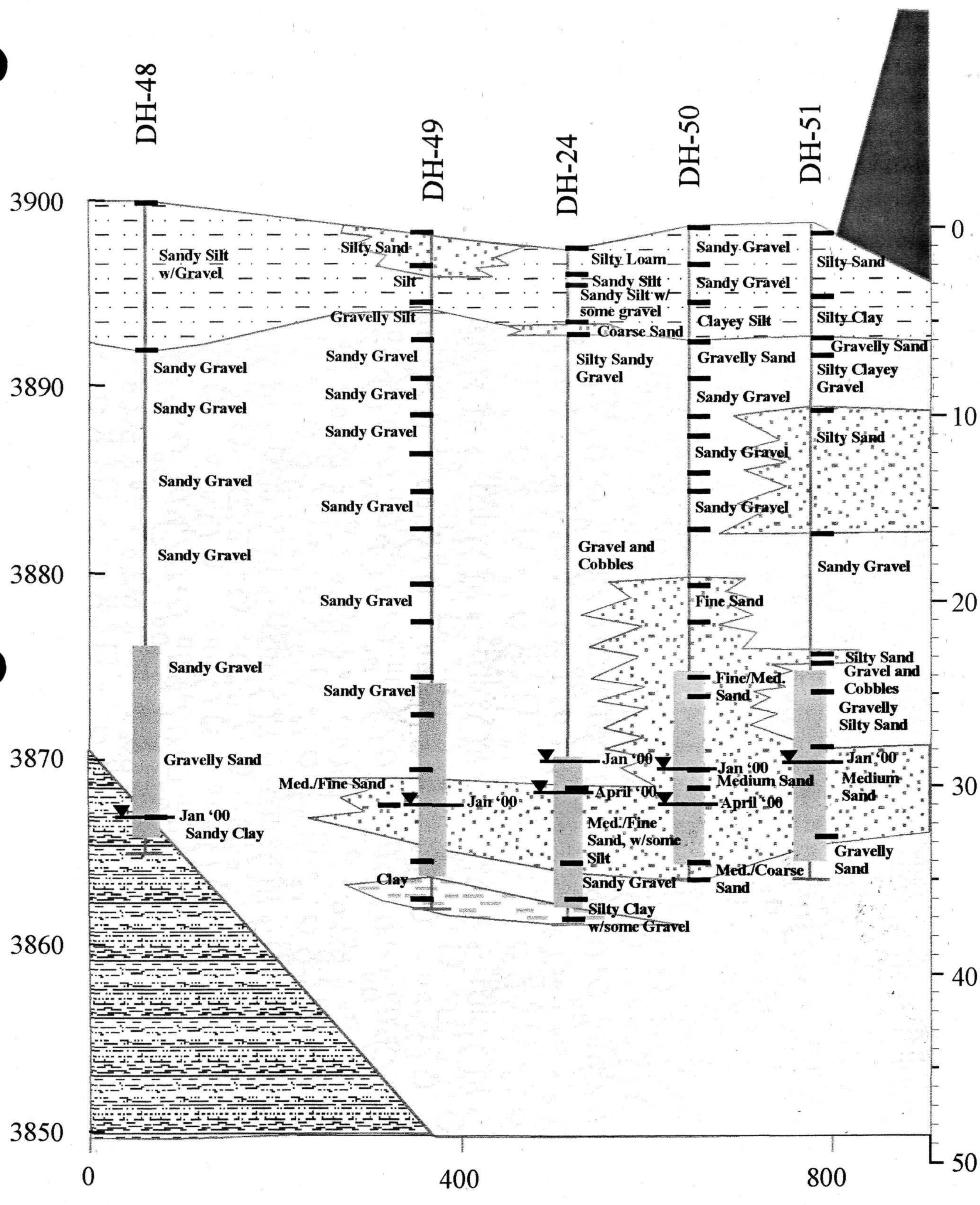
Site Code	Sample Date	Water Depth	Eh	Oxygen (FLD)	pH	pH (LAB)	SC (LAB)	SC (FLD)	Temp.	Ca	Mg	Na	K	HCO3	CO3	SO4	Cl	As	As+3	As+5	Cd	Fe	Fe (FLD)	Fe+2 (FLD)	Pb	Mn	Zn
Units		feet	illiVolt	mg/L	s.u	s.u.	umhos/cm at 25 C		Celcius	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Phase I SPAR-1 & SPAR-2 Sparge System																											
DH-50	5/18/00	33.68	331	0.97	6.77			2540	13.9									12			<0.0005	<0.025	0.01	0.01	<0.0025	2.2	0.54
STW-1	5/10/00	33.77	241	1.29	6.88	7.8	2890	2790	12.7	68	16	521	13	256	0.5	921	229	46	46	3.8	<0.0005	0.13	0.2	<0.05	<0.0025	2.5	0.16
	5/18/00	33.75	224	1.18	6.99		-	2940	13.6									48			0.001	0.17	0.2	0.17	<0.0025	2.5	0.22
STW-2	5/10/00	33.04	274	1.07	6.84	7.8	2620	2650	12.4	78	19	464	13	268	0.5	856	178	24	14	11	<0.0005	<0.025	0.1	0.2	<0.0025	2.7	0.16
	5/18/00	33	287	1.05	6.96			2640	13.5								-	27	-		<0.0005	<0.025	0.03	0.01	<0.0025	2.7	0.23
STW-3	5/10/00	33.47	319	1.42	6.82	8	2550	2680	11.9	73	18	452	13	259	0.5	842	188	22	12	13	<0.0005	<0.025	0.1	<0.05	<0.0025	2.9	0.12
	5/18/00	33.42	274	1.02	6.95			2580	13.7									25			<0.0005	0.05	0.09	0.07	<0.0025	3.3	0.2
STW-4	5/10/00	32.78	216	1.28	6.76	7.5	2650	2670	12.3	70	18	458	13	251	0.5	844	182	37	37	3.1	<0.0005	0.49	0.5	0.7	<0.0025	3.2	0.25
	5/18/00	32.75	204	1	6.96			2670	13.7									40			<0.0005	0.56	0.62	0.61	<0.0025	3.4	0.34
STW-5	5/10/00	32.7	316	1.38	6.69	7.8	2590	2720	12.1	92	23	417	12	271	0.5	875	187	17	8.7	9.8	<0.0005	<0.025	0.1	<0.05	<0.0025	2.7	0.2
	5/18/00	32.64	309	1.15	6.83			2620	13.5									19			0.002	<0.025	0.05	0.03	<0.0025	2.8	0.26
STW-6	5/10/00	32.91	301	1.45	6.91	7.8	2560	2700	12.2	66	15	453	12	239	0.5	806	182	27	15	14	<0.0005	0.094	0.2	0.1	<0.0025	2.6	0.1
	5/18/00	32.87	282	0.96	7.05			2560	13.8									28			<0.0005	<0.025	0.07	0.05	<0.0025	2.7	0.16
SP-1	Not Sampled																										
SP-2	Not Sampled																										
Phase I SPAR-3 Sparge System																											
DH-24	5/1/00		459	3.62	6.01	6	1116	1147	11.9	49	21	113	13	62	<1.0	435	44	19	17	3.5	0.13	12			<0.005	7.4	4.7
	8/3/00	27.74	247	0.93	6.17	6	1066	1120	13.9	46	18	109	12		<0.5		30	20	14	5.9	0.12	11		10.4	<0.0025	6.7	4.3
	8/16/00	27.83	277	0.93	6.4			1031	13.4									16	13	2.3			8	8.2			
EH-60	5/3/00	22.82	384	3.8	6.7	6.9	1946	2020	12.3	85	25	268	12	262	<1.0	669	132	11	8.6	3.6	0.001	0.23			<0.005	21	0.034
	8/3/00	20.86	287	1.08	6.28	7.3	1902	2050	12.5	81	23	264	11	256	<0.5	810	110	11	8.2	4.5	<0.0005	0.18		0.16	<0.0025	19	0.023
	8/16/00	20.99	288	0.73	6.1			1432	12.6									11	7.9	4.2			0.17	0.16			
SP-3	8/3/00	31.79	255	0.94	6.17	6	1080	1116	13.8	49	19	113	13	49	<0.5	579	36	25	21	0.94	0.12	12		11.8	<0.0025	7	4.4
	8/16/00	33.18	275	1.33	6.9			1098	13.6									19	17	1.4			4.6	4.2			

Note: Phase I SPAR-1 test began 5/23/2000 and Phase I SPAR-3 test began 8/19/2000

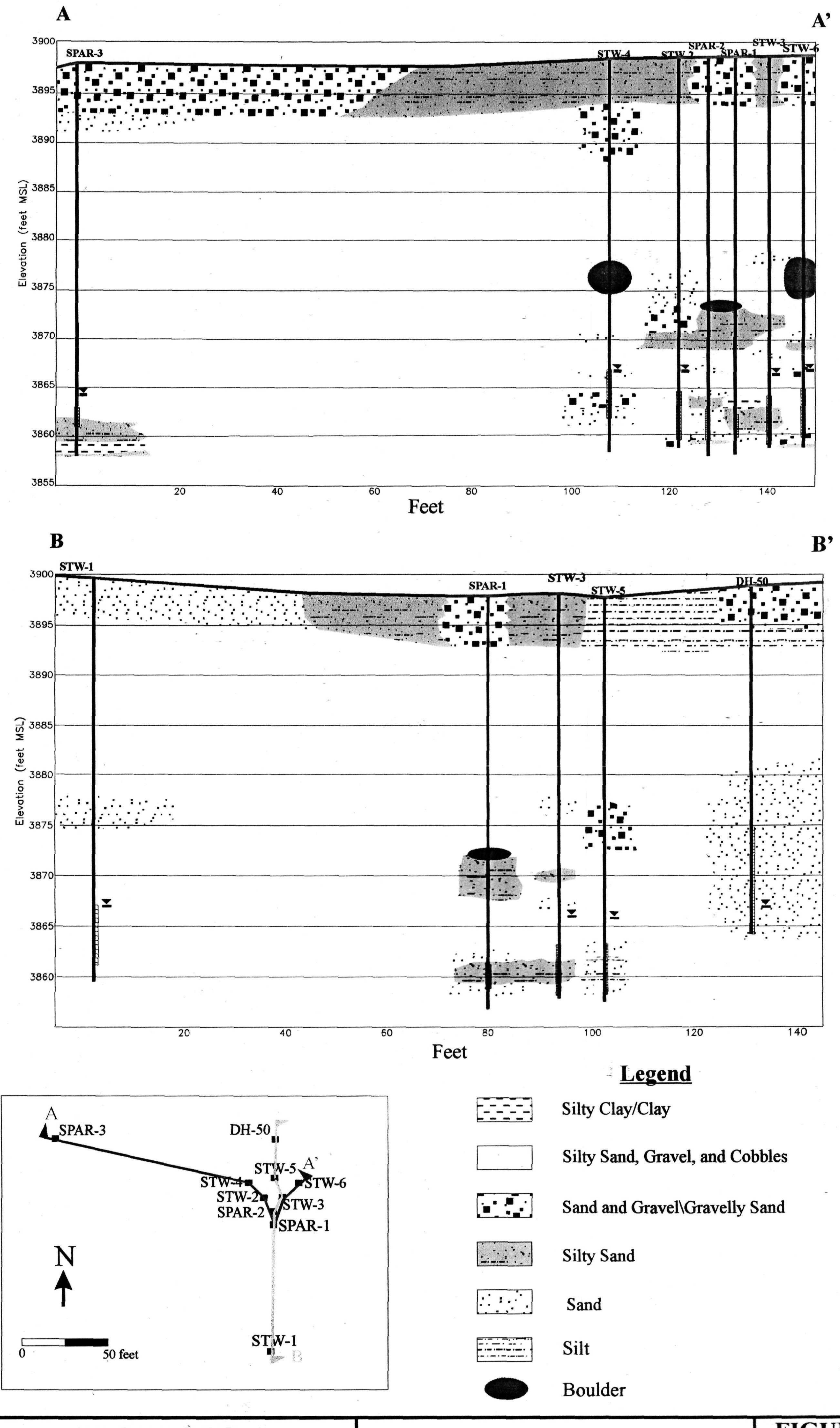
FIGURES



AIR SPARGING PILOT TEST REPORT EAST HELENA FACILTY	NOVEMBER/DECEMBER 1999 DISSOLVED ARSENIC CONCENTRATIONS IN SHALLOW GROUNDWATER	FIGURE 2-1



AIR SPARGING PILOT TEST REPORT EAST HELENA FACILTY	GEOLOGIC CROSS SECTION IN AREA OF AIR SPARGING	FIGURE 2-2



AIR SPARGING PILOT TEST REPORT EAST HELENA FACILTY	GEOLOGIC CROSS SECTIONS AT SPARGE WELLS	FIGURE 2-4

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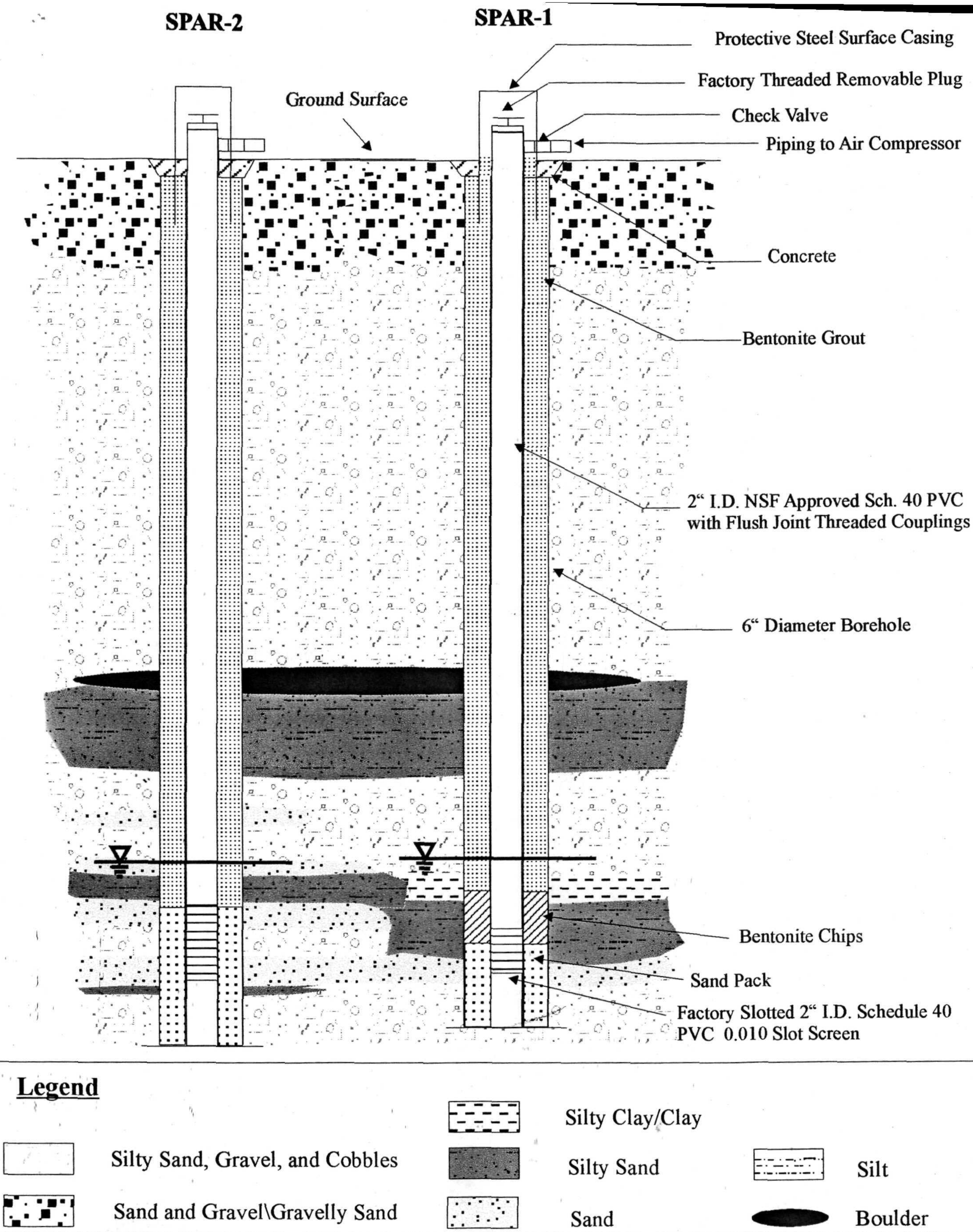

AIR SPARGING PILOT TEST REPORT EAST HELENA FACILTY	WELL CONSTRUCTION AND STRATIGRAPHY FOR SPAR-1 AND SPAR-2	FIGURE 2-5

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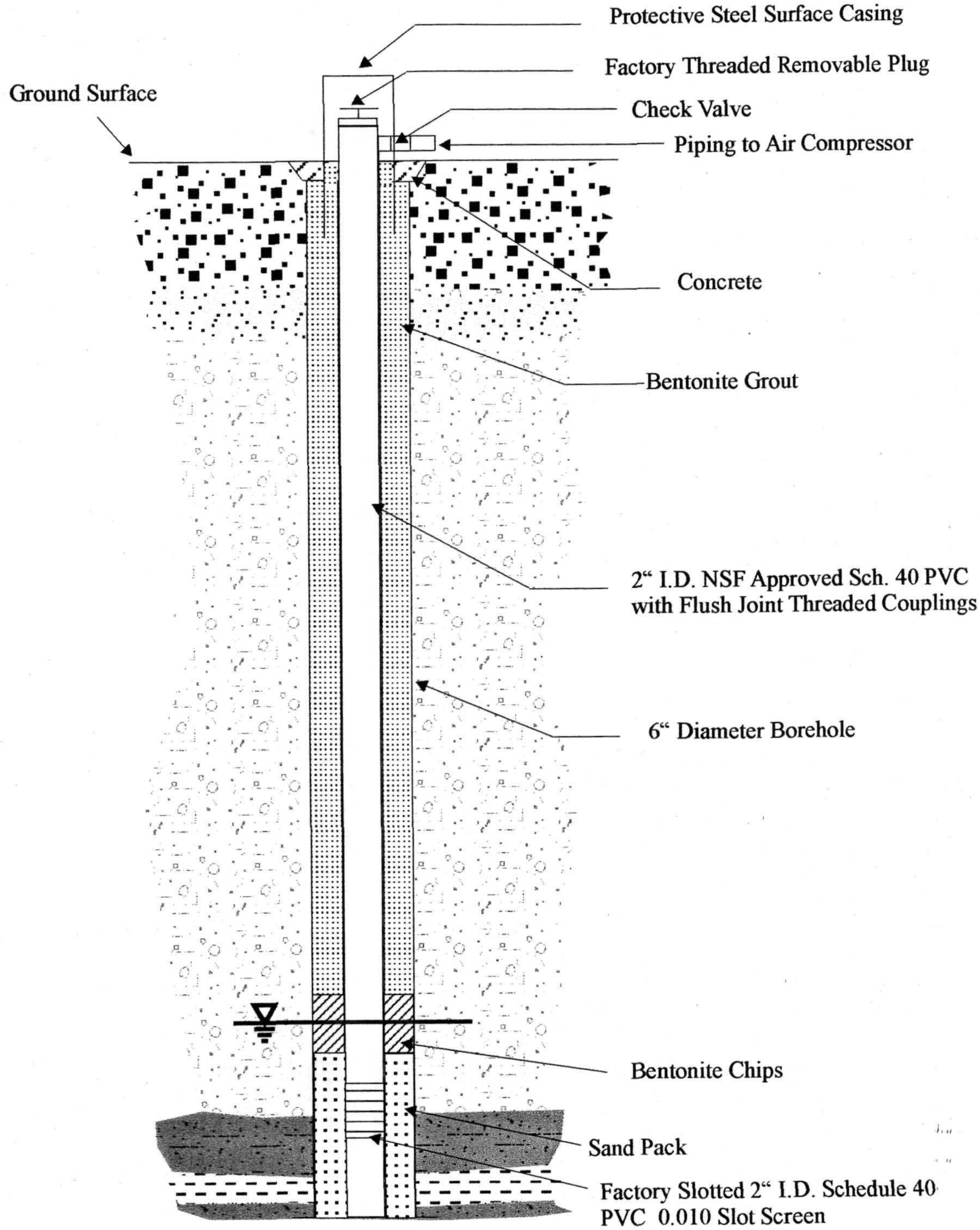
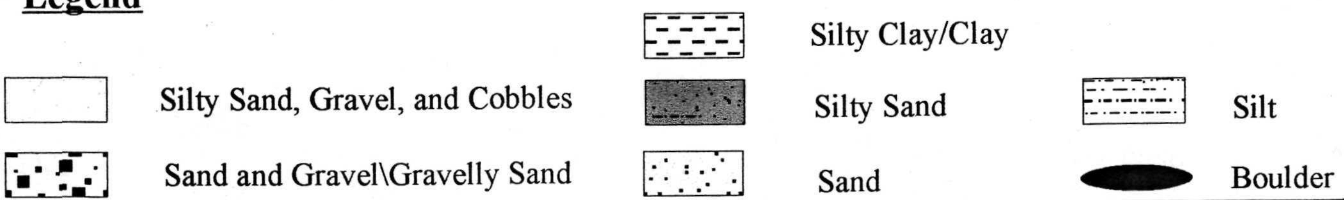
SPAR-3



Legend



AIR SPARGING PILOT TEST REPORT EAST HELENA FACILTY	WELL CONSTRUCTION AND STRATIGRAPHY FOR SPAR-3	FIGURE 2-6

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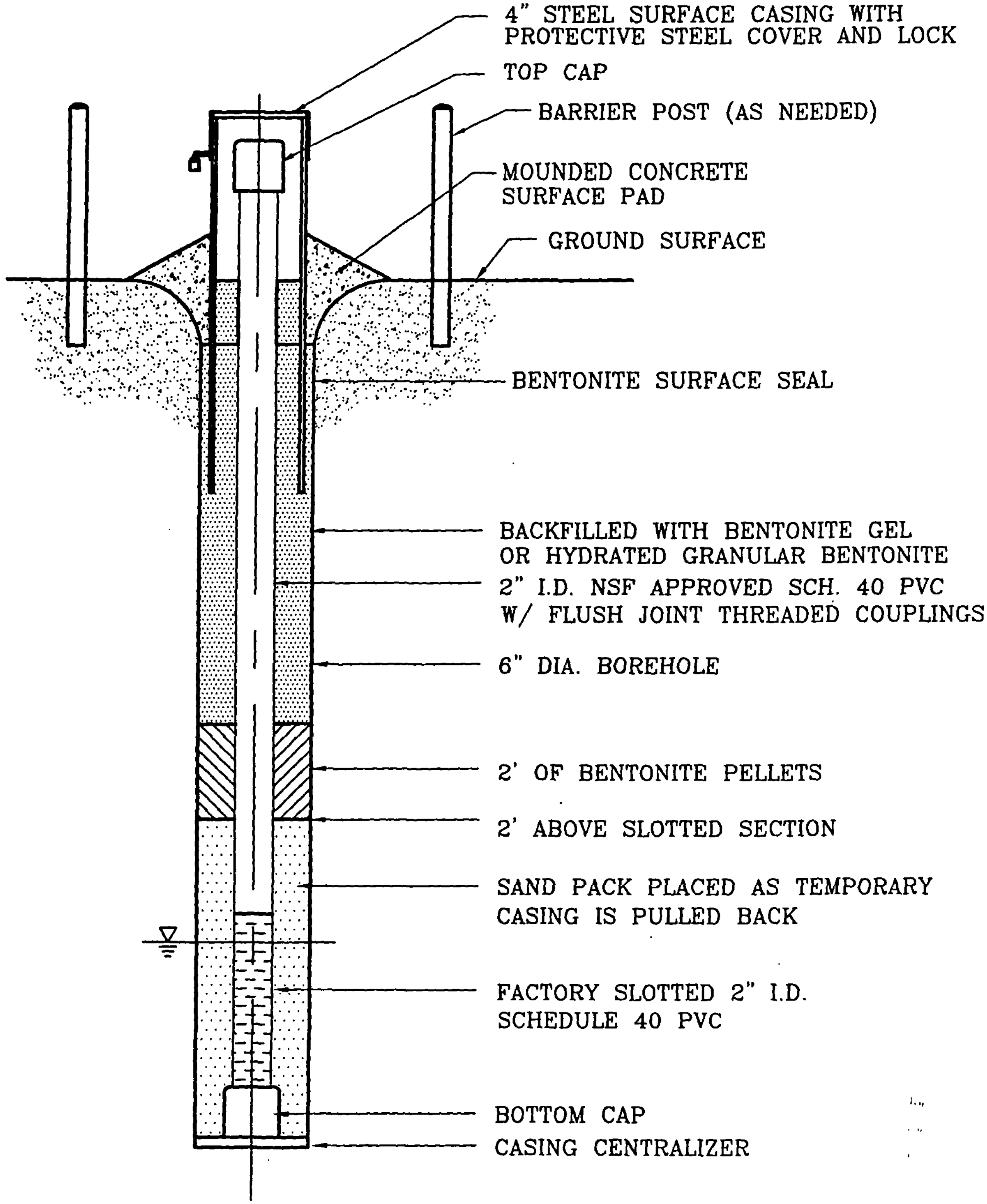

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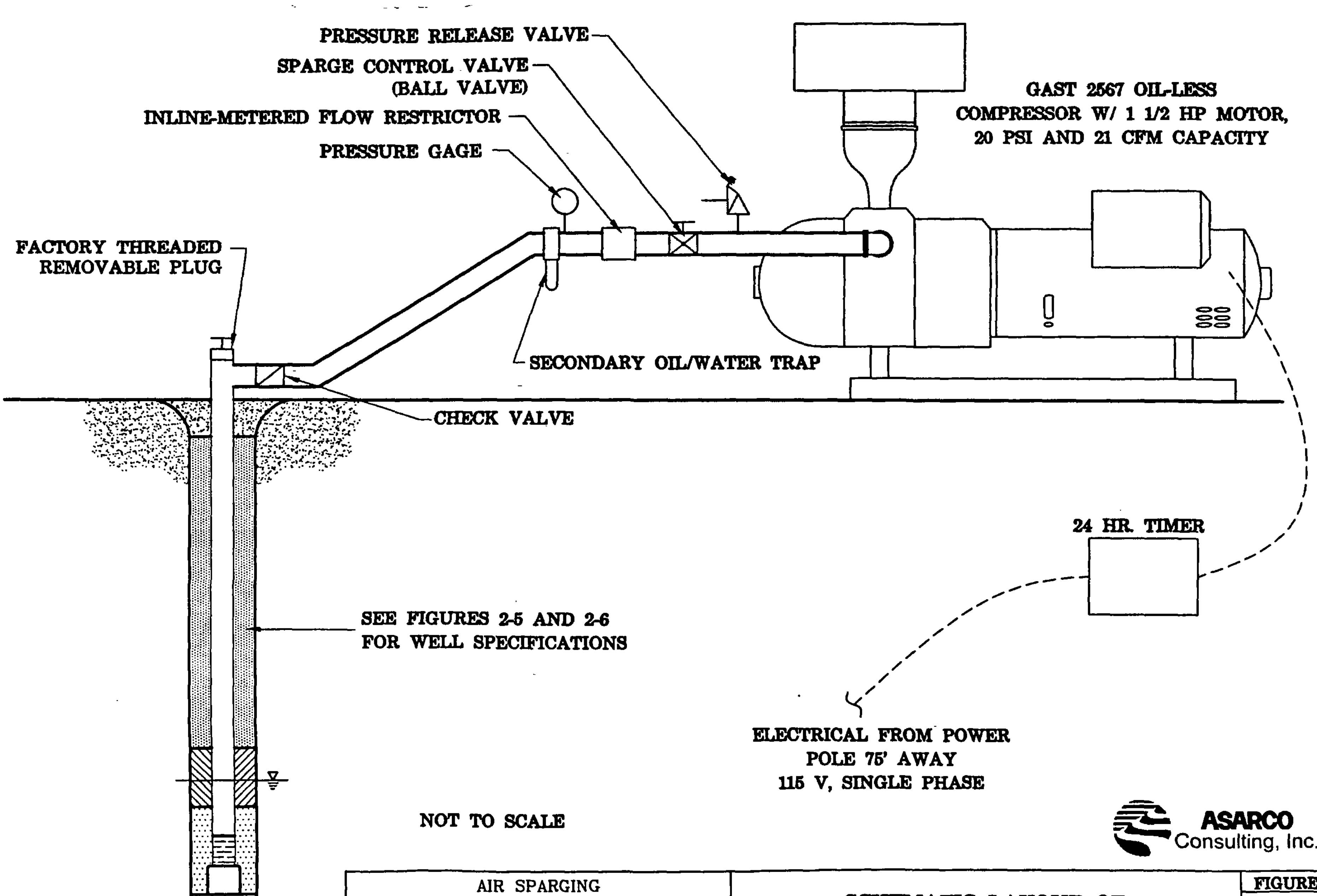
NOT TO SCALE

AIR SPARGING PILOT TEST REPORT EAST HELENA FACILTY	TYPICAL SHALLOW MONITORING WELL CONSTRUCTION	FIGURE 2-7

UPDATE TIME: 11:00am
\ \ \OOPG\TAC\041403\\:\Land Projects\East Helena-04-11-03\East Helena-04-11-03-T003.dwg



ASARCO Consulting, Inc.

AIR SPARGING PILOT TEST REPORT EAST HELENA FACILTY	SCHEMATIC LAYOUT OF AIR SPARGE SYSTEM	FIGURE 2-8

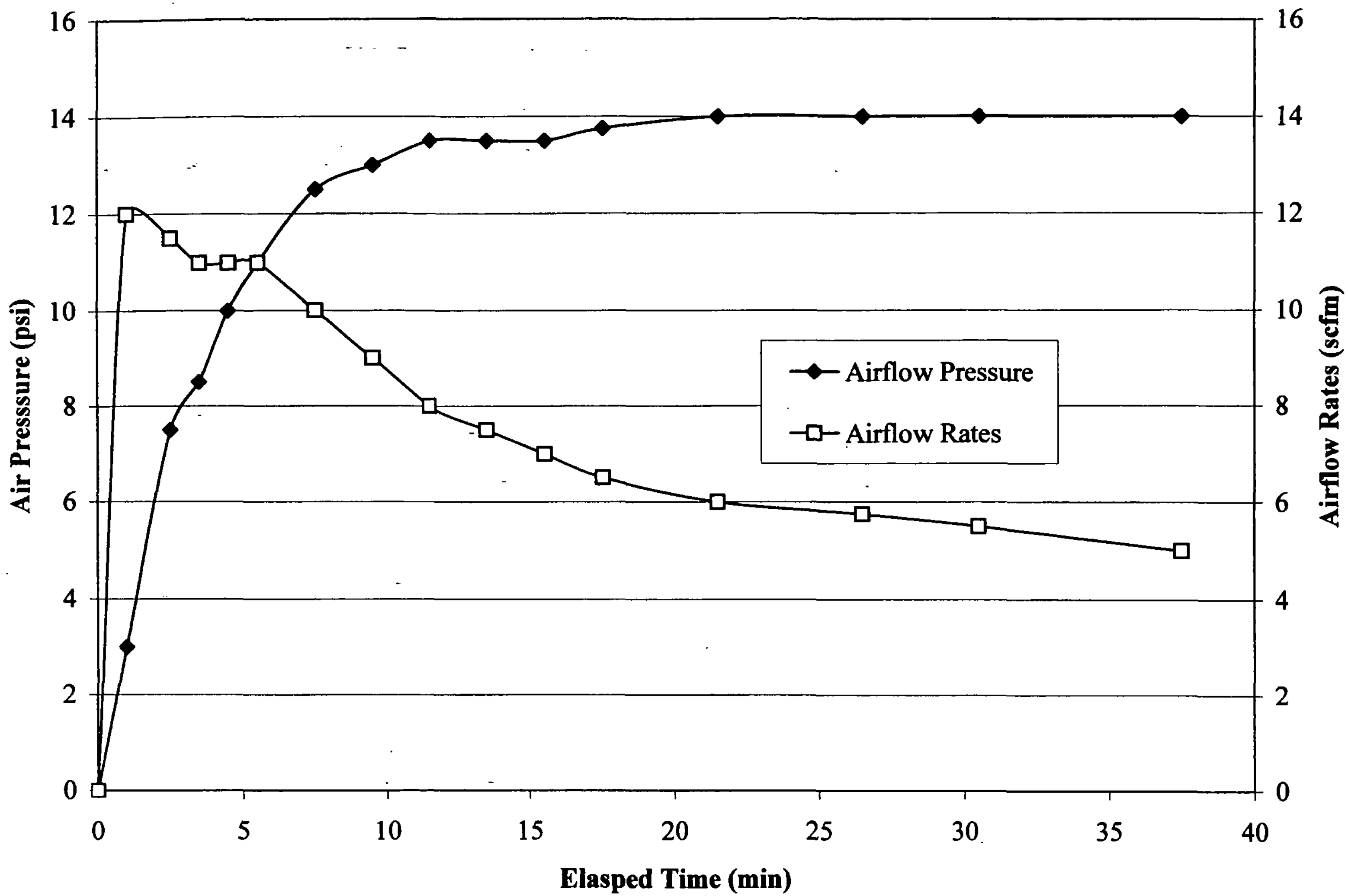


FIGURE 2-9. SPAR-2 AIRFLOW RESPONSE AT SYSTEM START-UP

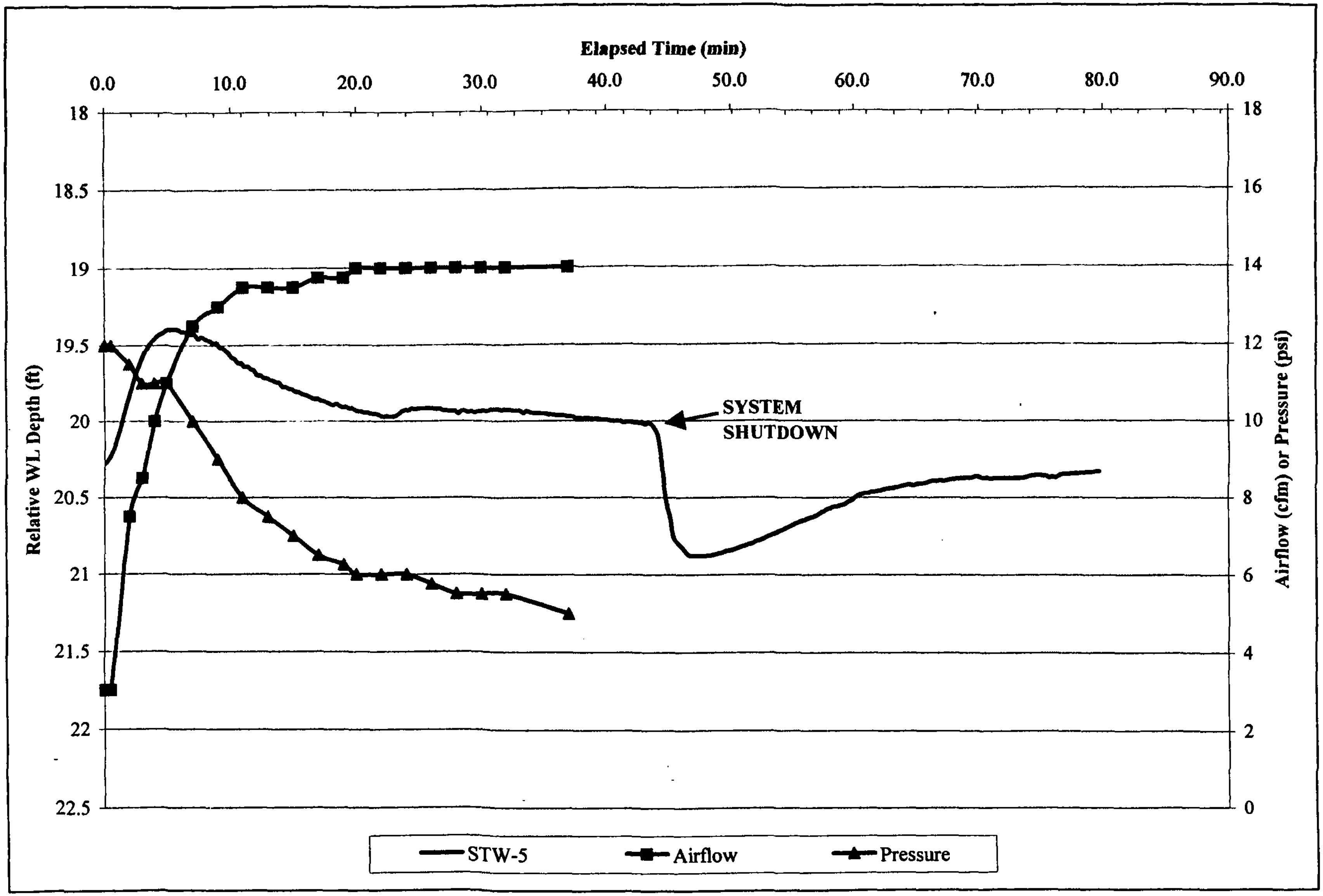
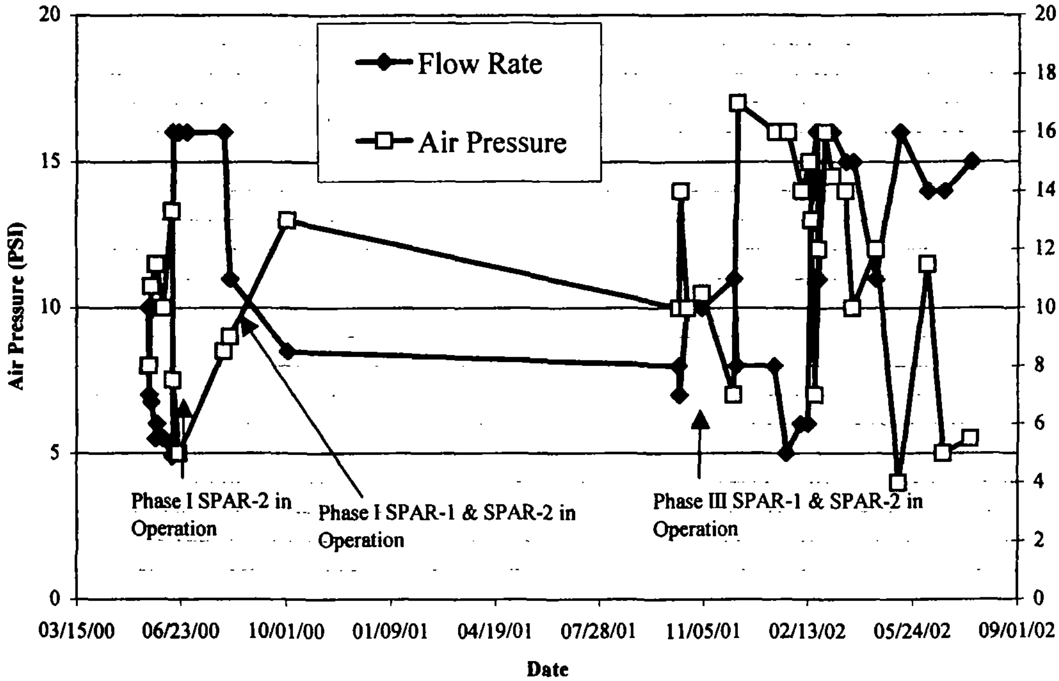


FIGURE 2-10. GROUNDWATER RESPONSE AT SYSTEM START-UP

SUMMARY OF AIRFLOW DATA
PHASE I AND PHASE III TEST- SPARGE 1 AND SPARGE 2



SUMMARY OF AIRFLOW DATA
PHASE I TEST AND PHASE III - SPARGE 3

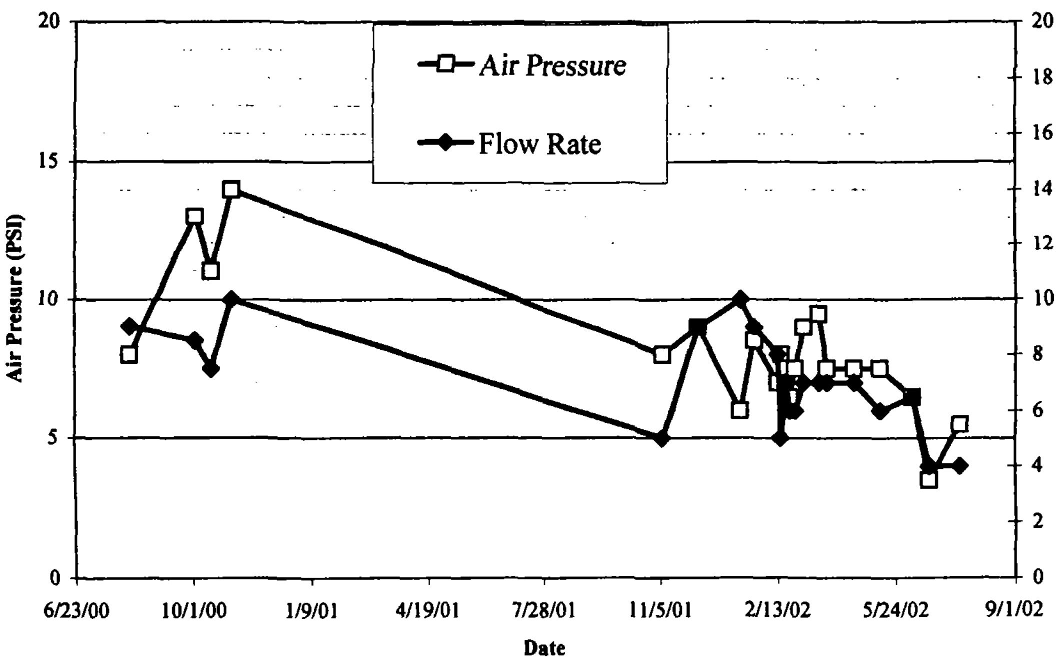


FIGURE 2-11. SUMMARY OF AIRFLOW DATA FROM SPARGE PILOT TESTS

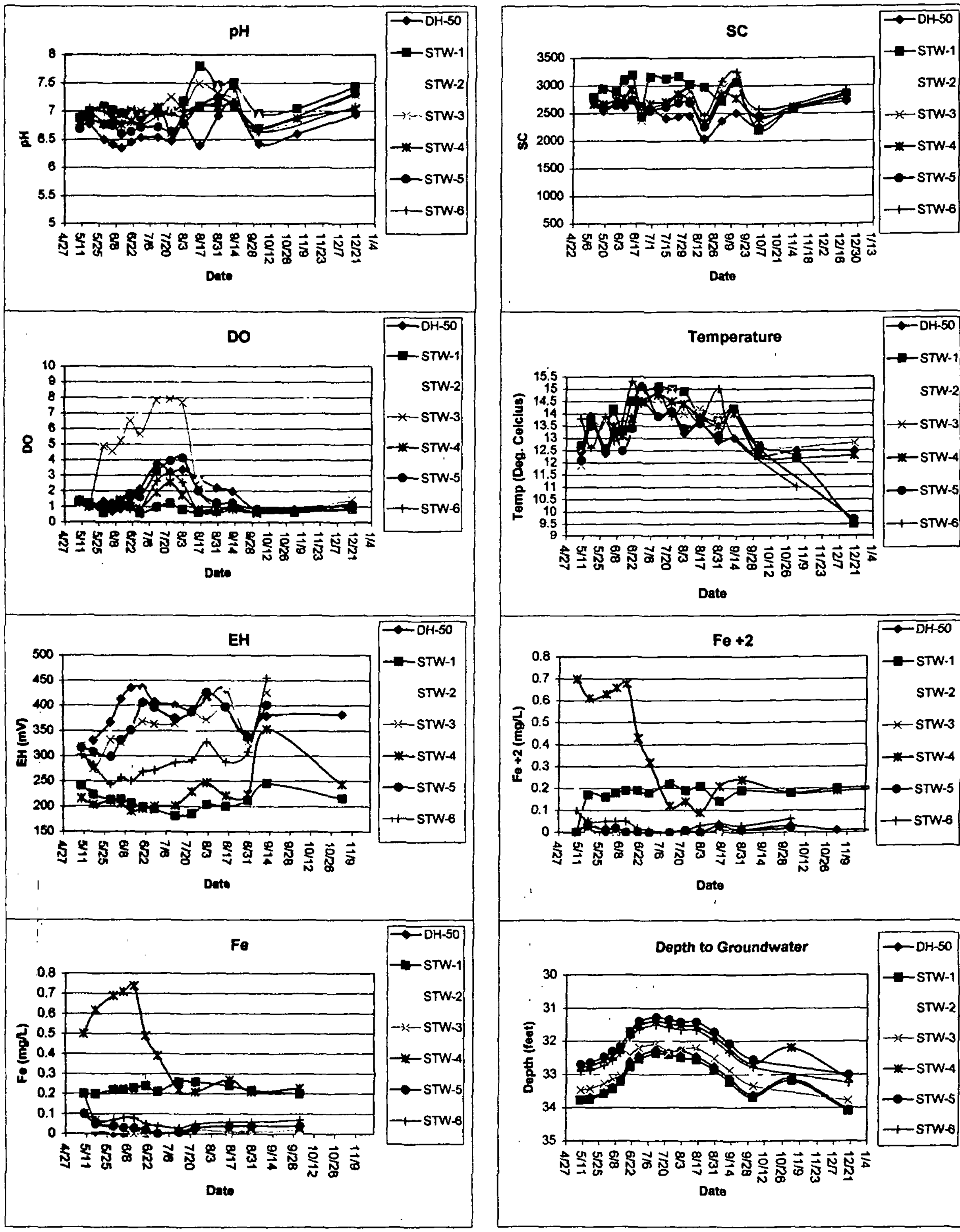


FIGURE 2-12. PHASE 1 SPAR 1 AND 2 PILOT TEST - FIELD PARAMETERS

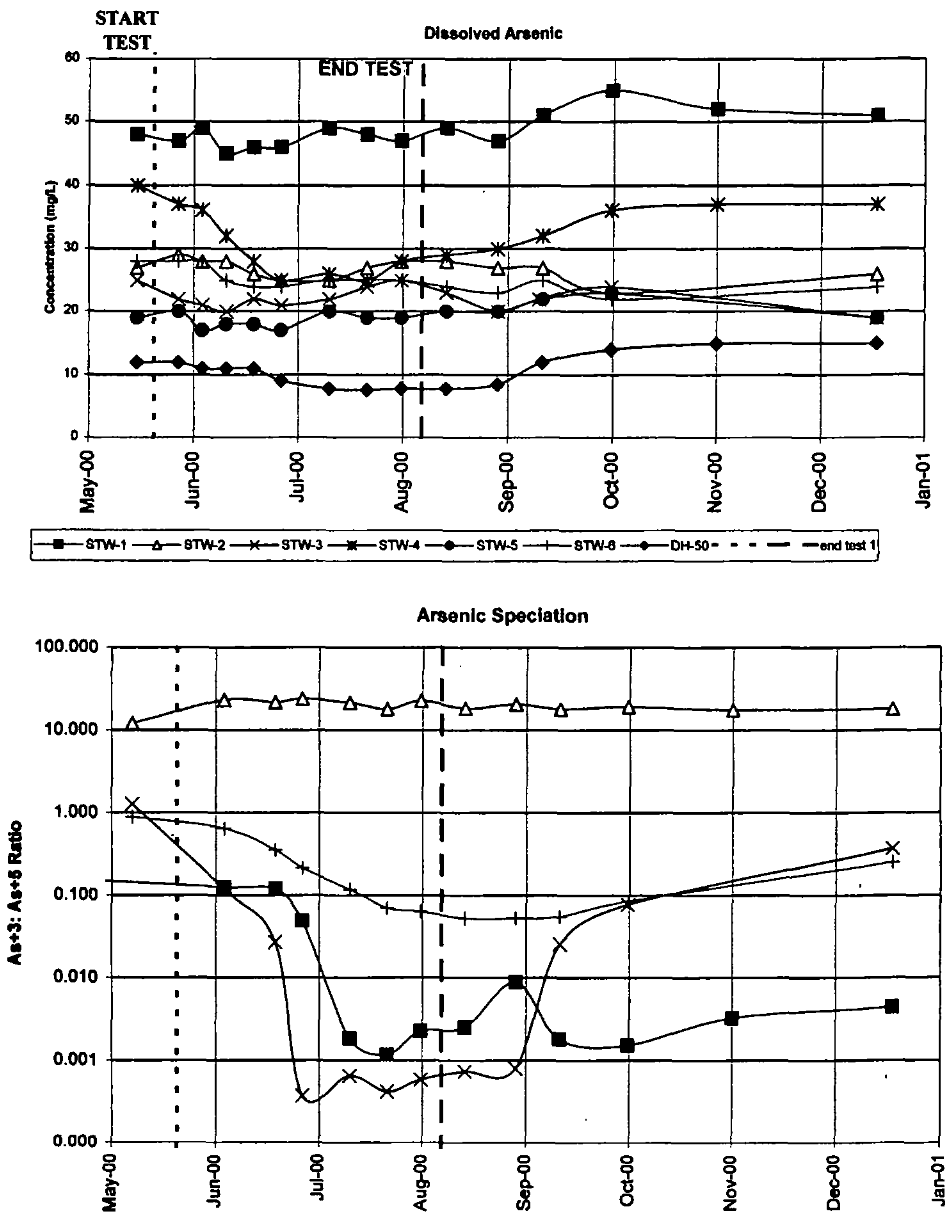


FIGURE 2-13. PHASE 1 SPAR-1 AND 2 PILOT TEST - ARSENIC CONCENTRATION GRAPHS

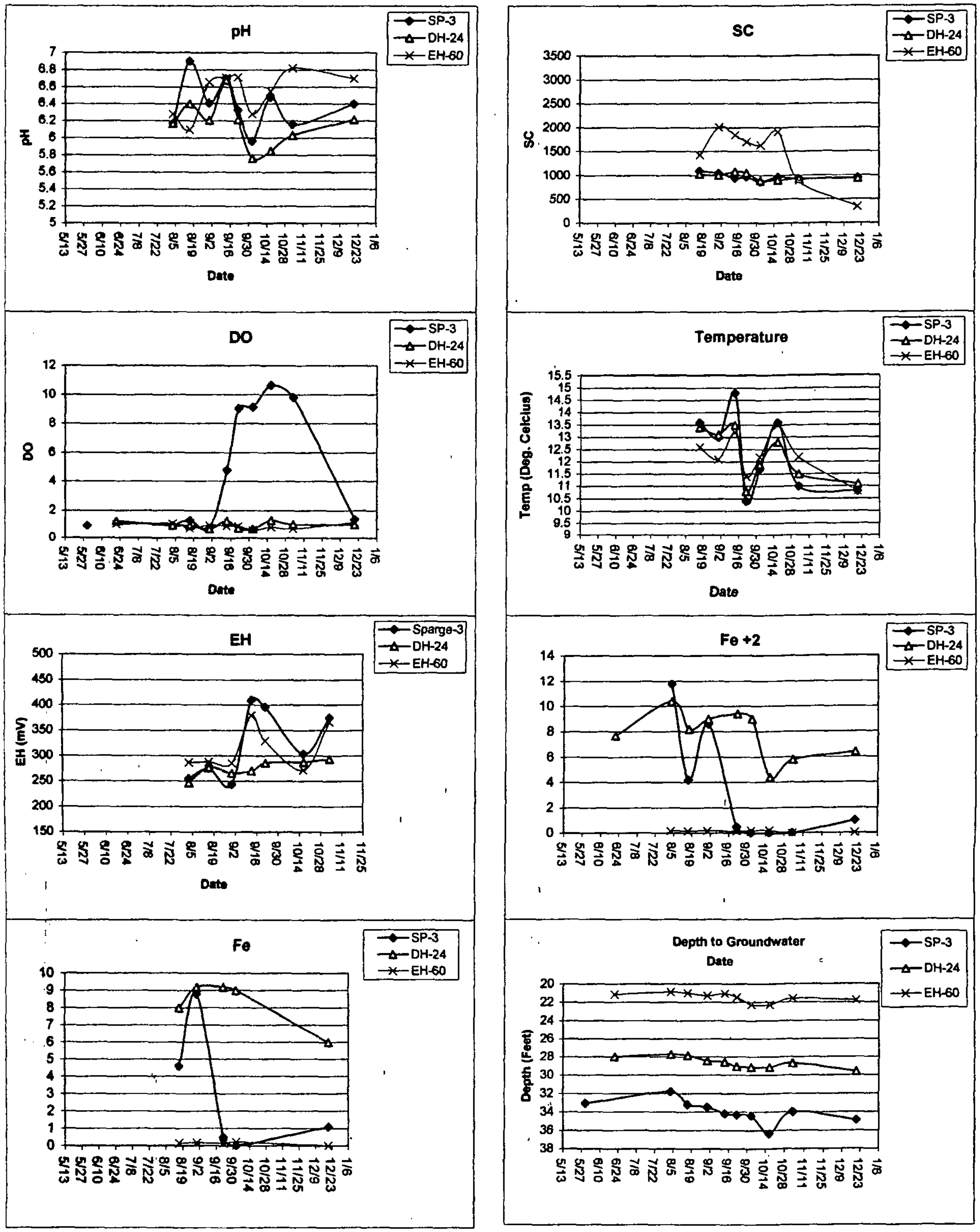


FIGURE 2-14. PHASE 1 SPAR-3 PILOT TEST - FIELD PARAMETERS

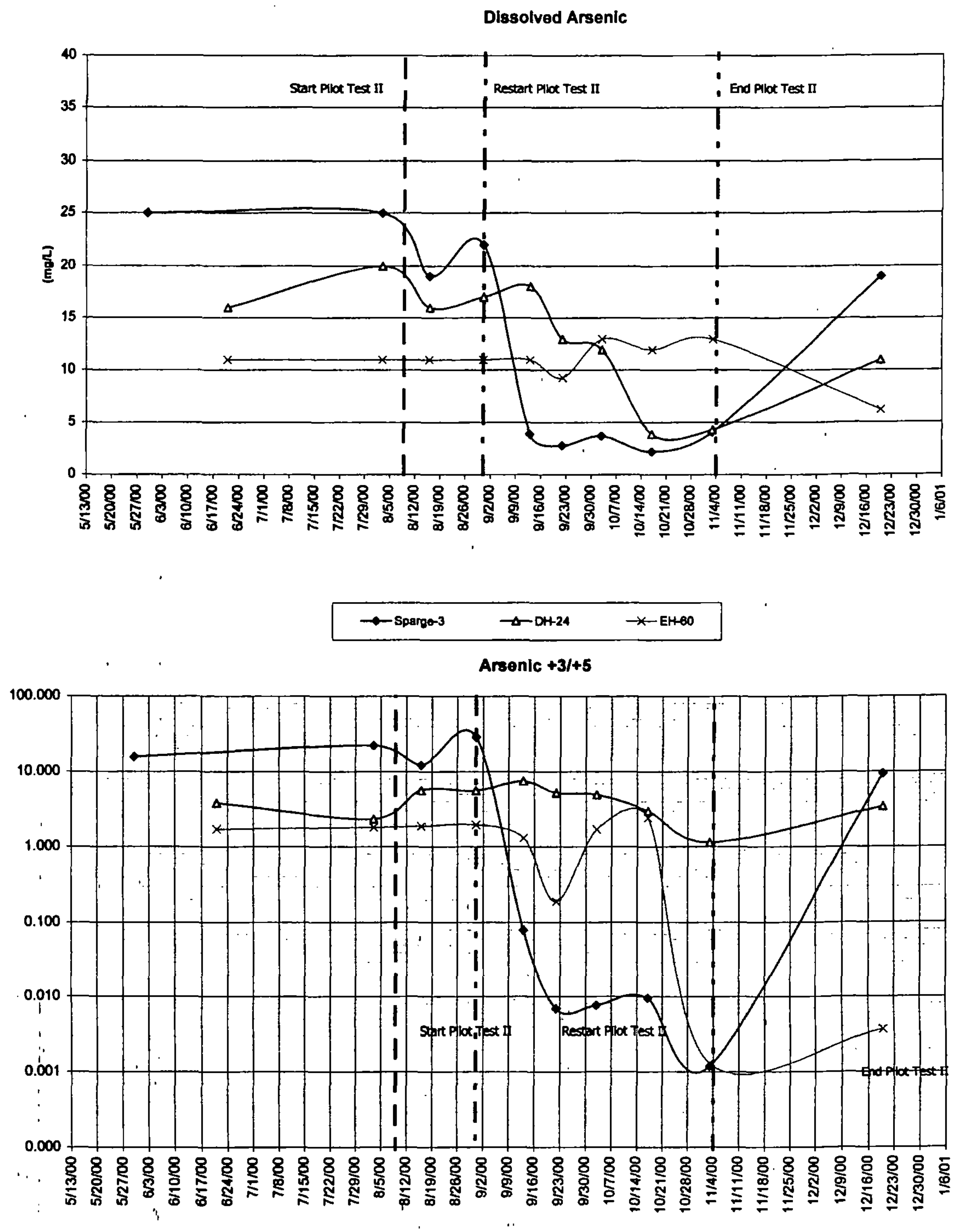
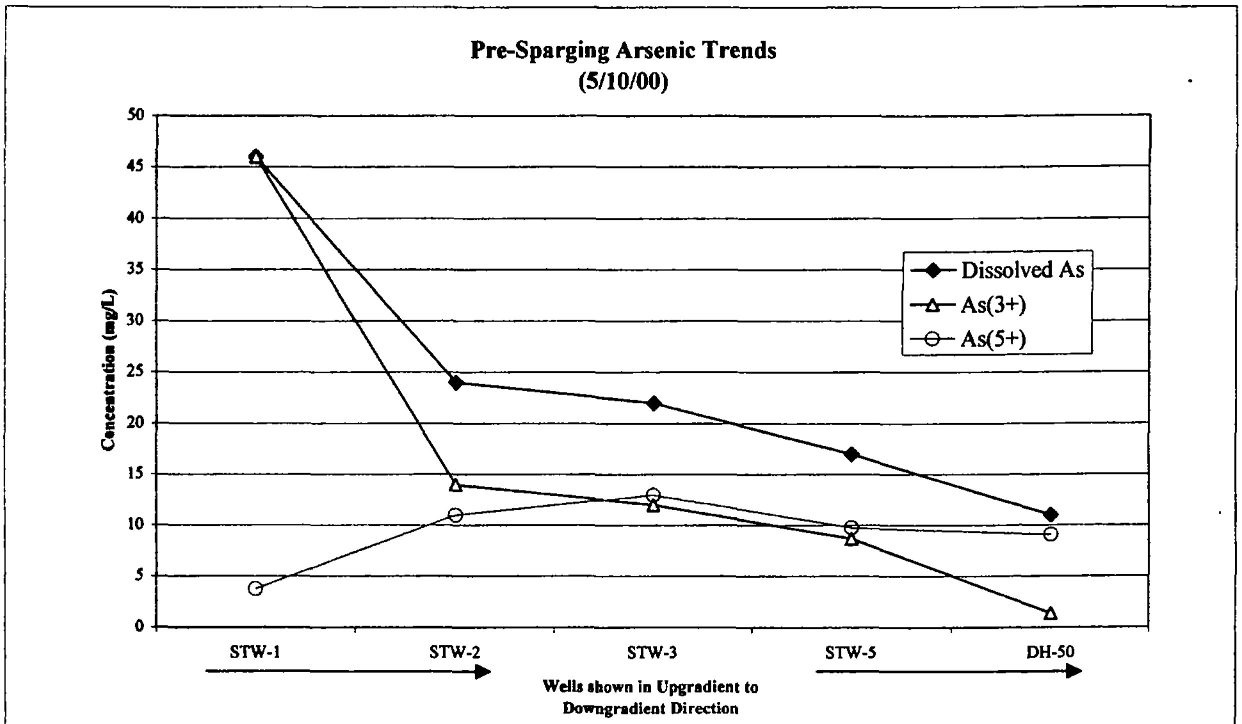


FIGURE 2-15. PHASE I SPAR 3 - ARSENIC CONCENTRATION GRAPHS



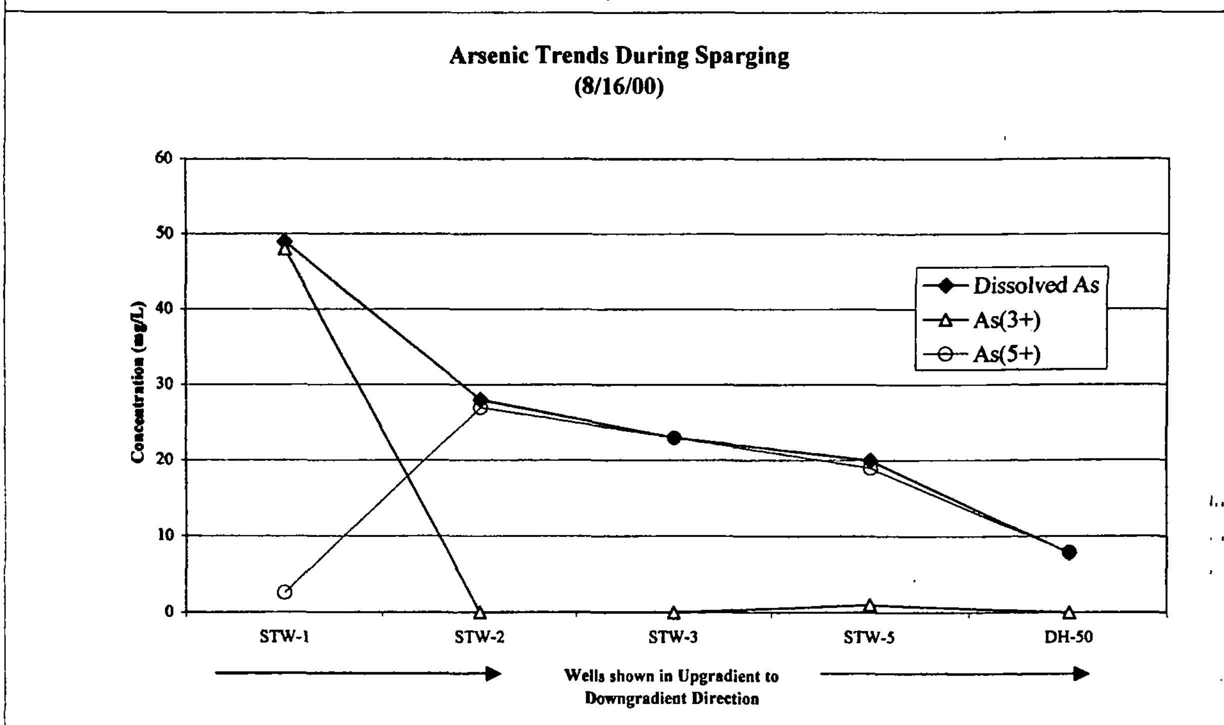
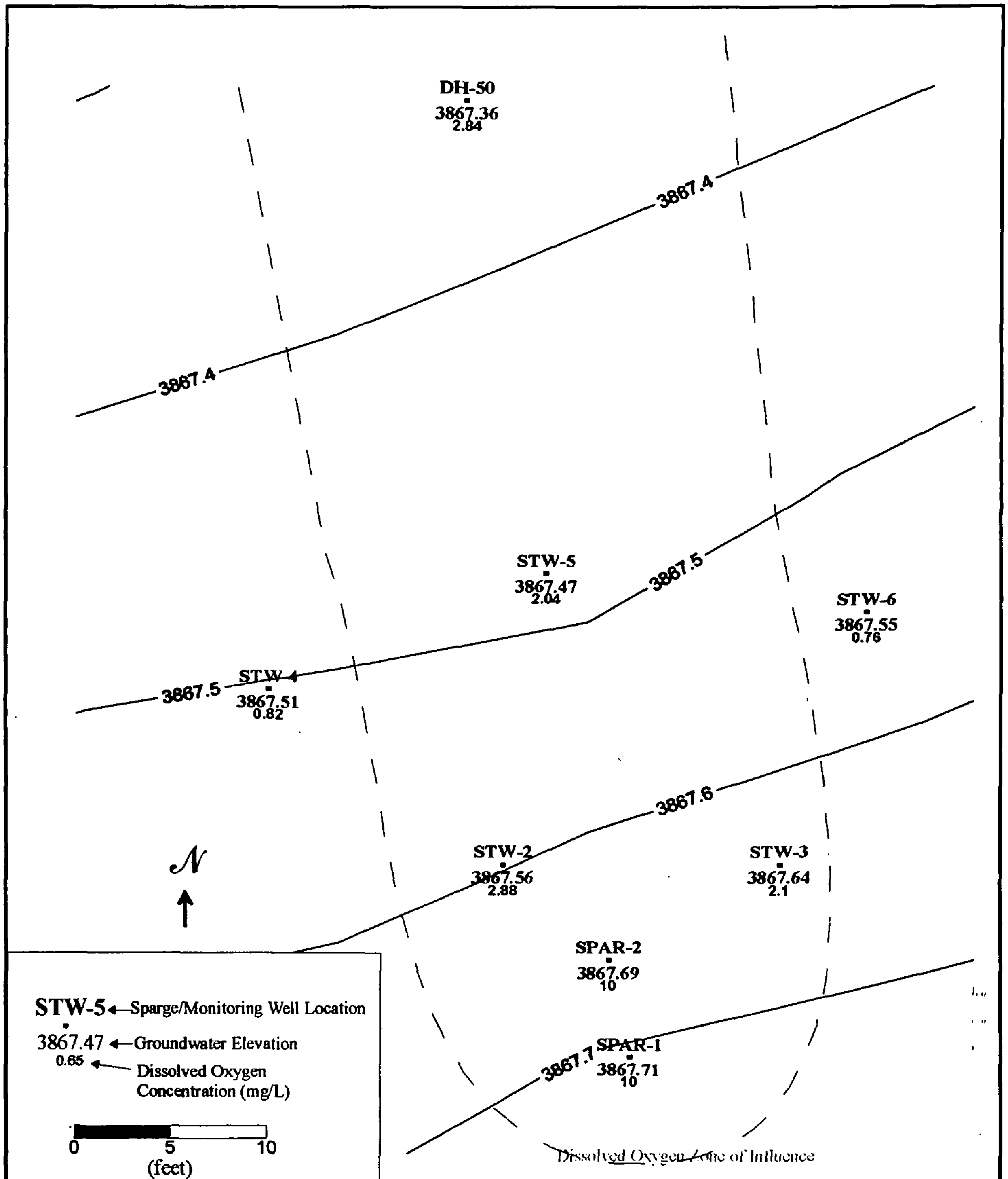
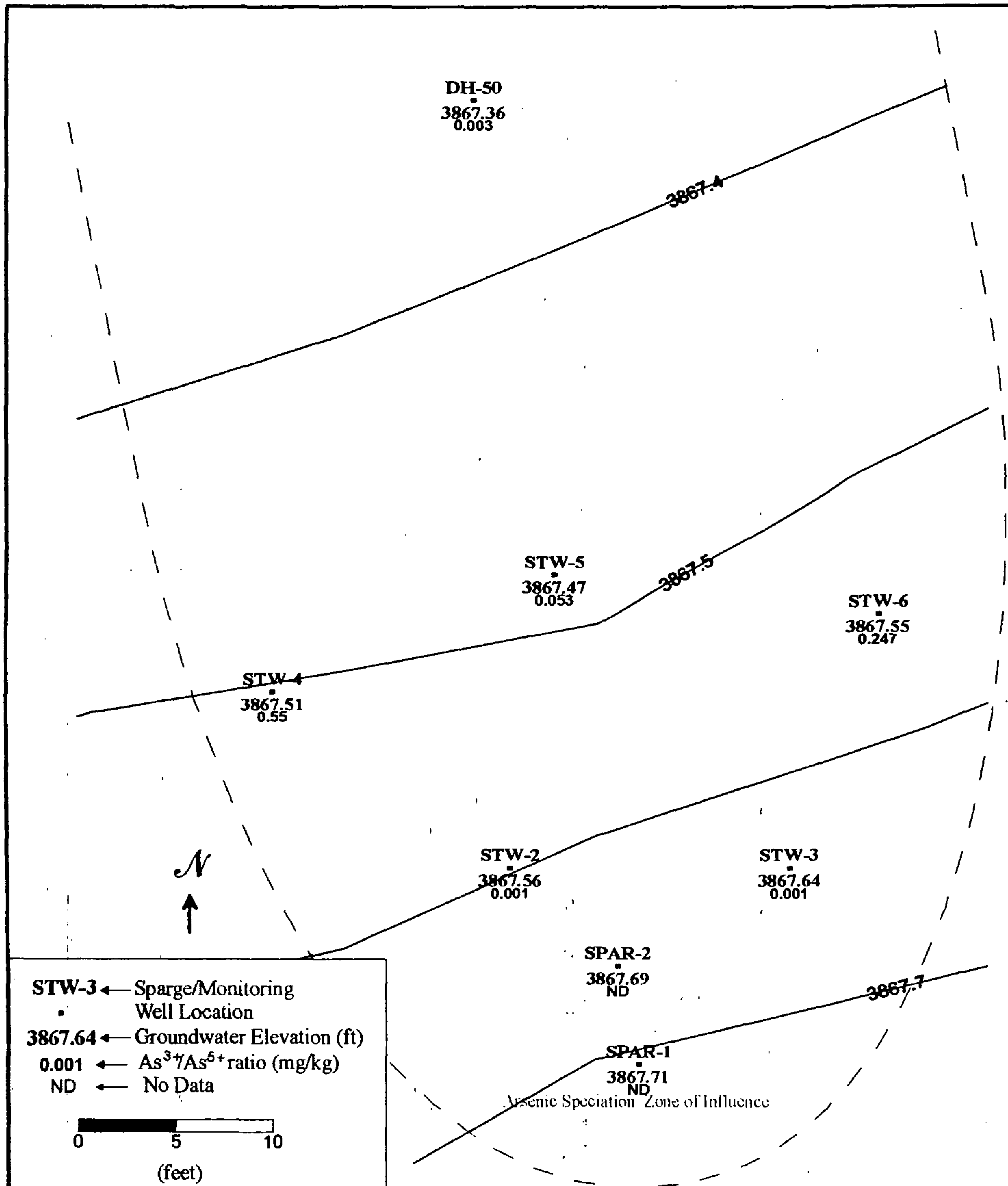


FIGURE 2-16. COMPARISON OF ARSENIC TRENDS IN GROUNDWATER PRE & POST TESTING



INTERIM MEASURES AIR SPARGING PILOT TEST SUMMARY REPORT	PHASE I SPAR 1 AND 2 PILOT TEST AUGUST 16, 2000 DISSOLVED OXYGEN ZONE OF INFLUENCE	FIGURE 2-17

K:/PROJECT/1257/RFI-2002/SPARGE/OXYGENMAP.srf



INTERIM MEASURES AIR SPARGING PILOT TEST SUMMARY REPORT	PILOT TEST I - AUGUST 16, 2000 ARSENIC SPECIATION (AS 3+/5+) ZONE OF INFLUENCE	FIGURE 2-18

K:/PROJECT/1257/RFI-2002/SPARGE/POTMAP3.srf

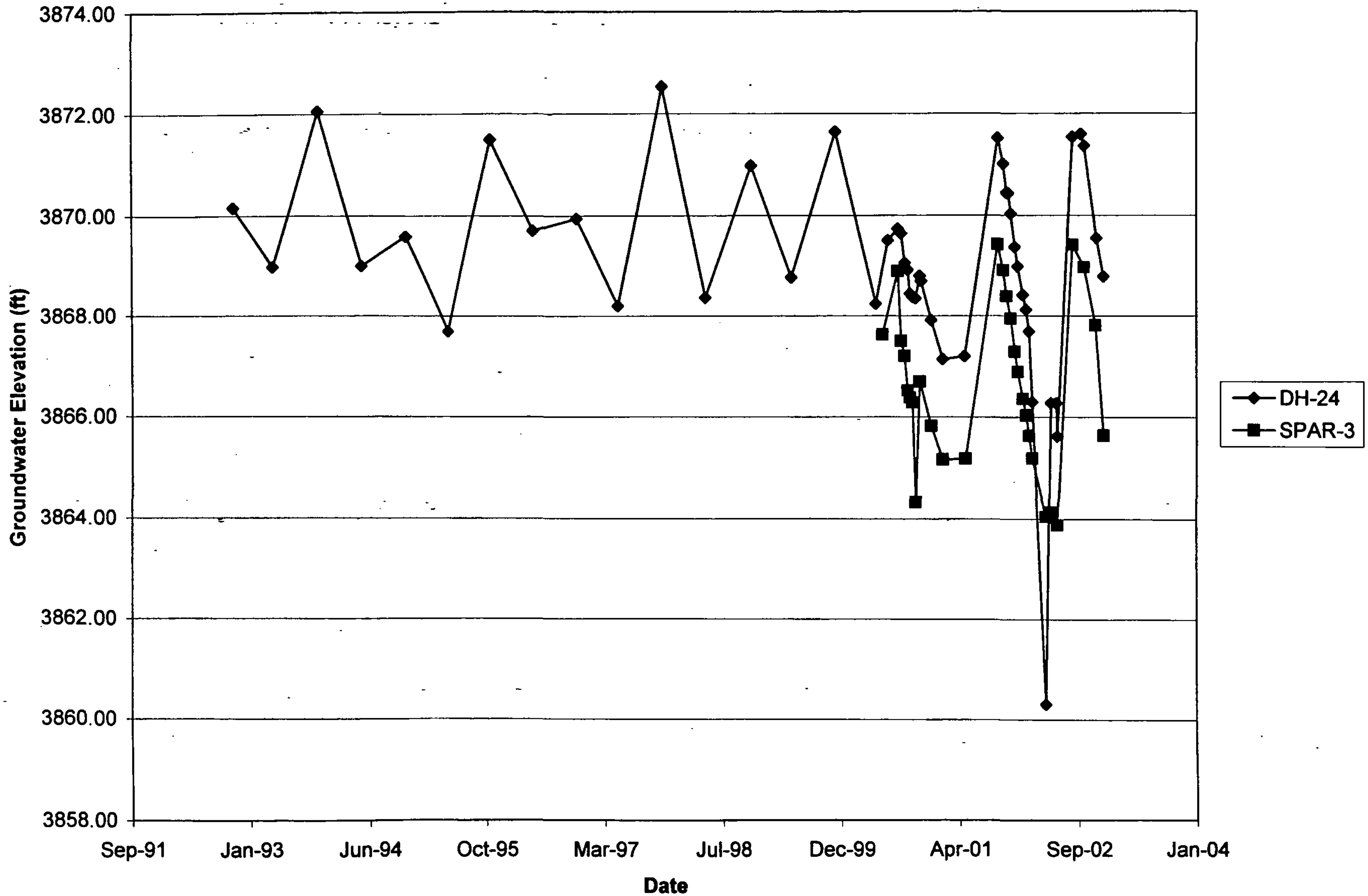
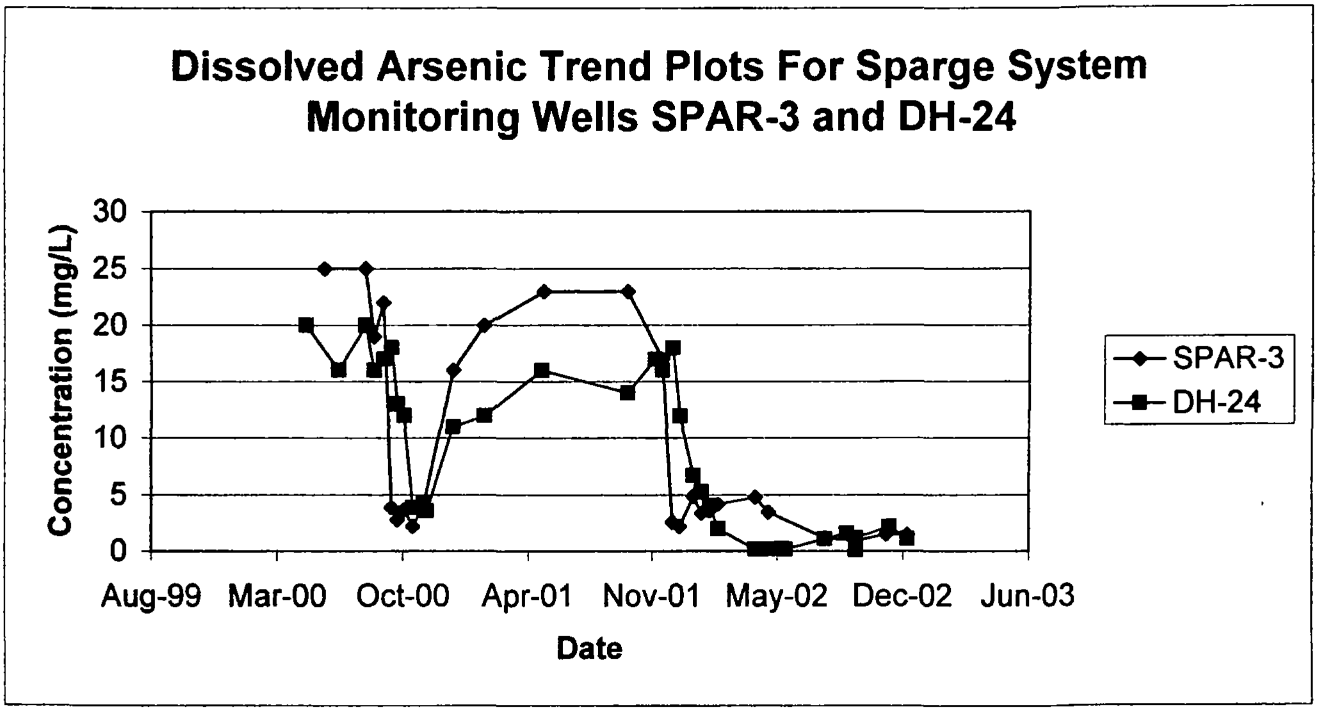


Figure 4-1. Water Level Trends at SPAR-3 Sparge System



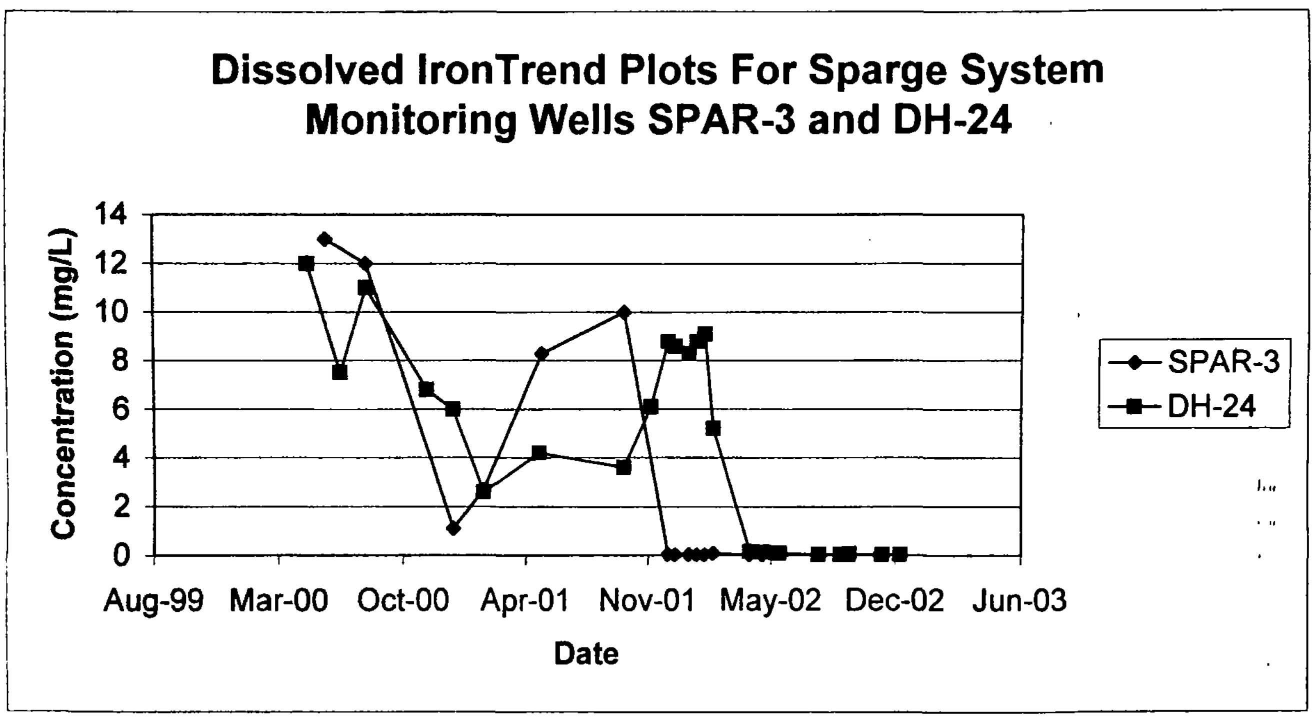
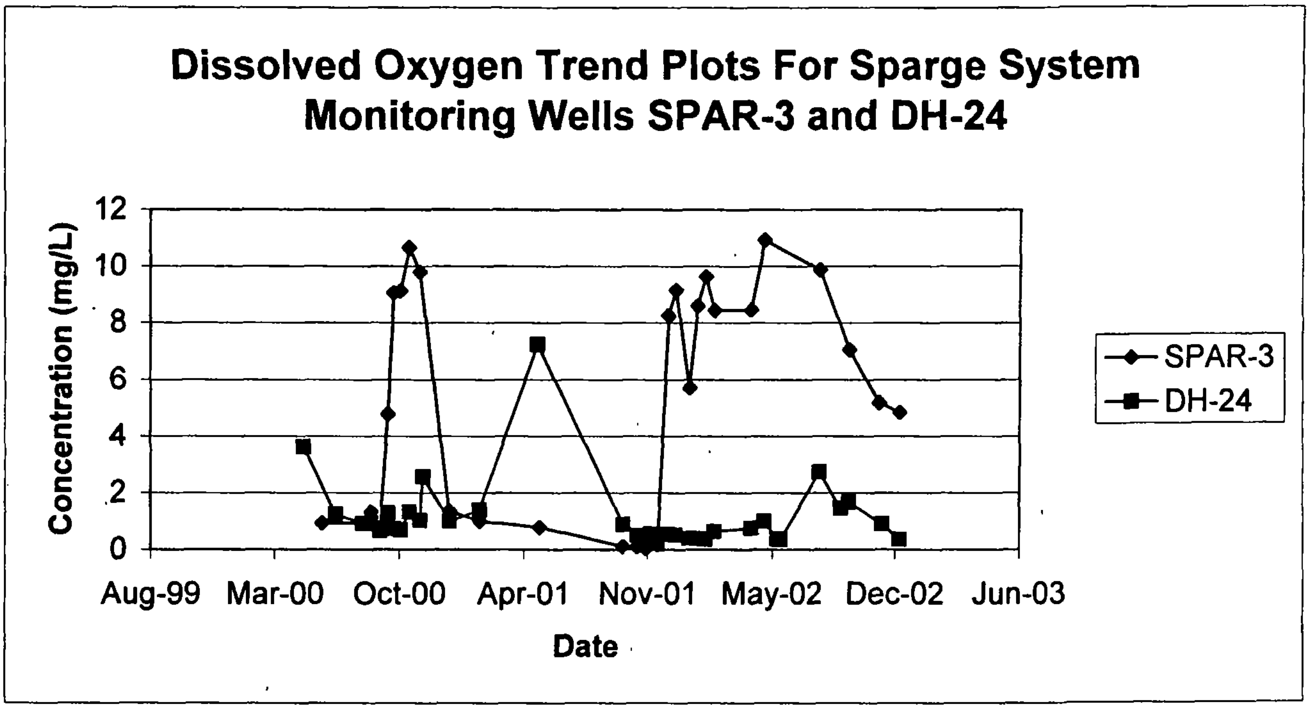


FIGURE 4-2. PHASE III WATER QUALITY TREND GRAPHS FOR SPAR-3 AND DH-24



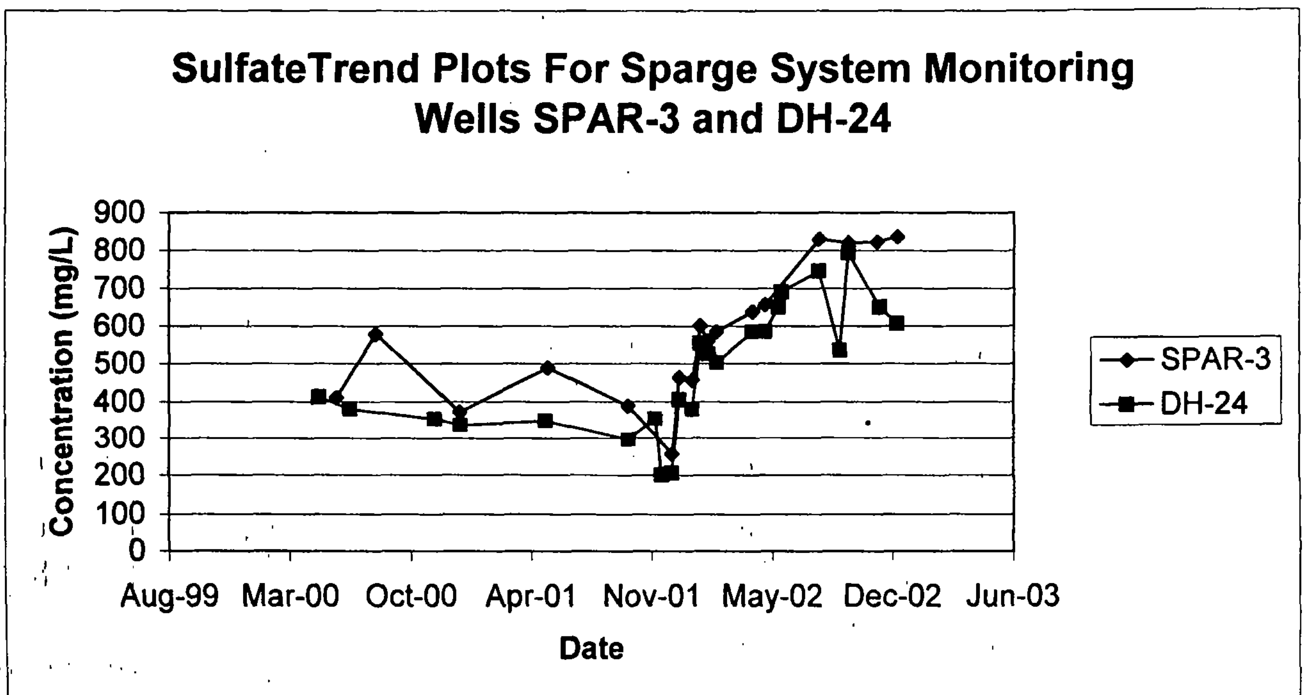


FIGURE 4-3. PHASE III WATER QUALITY TREND GRAPHS FOR SPAR-3 AND DH-24

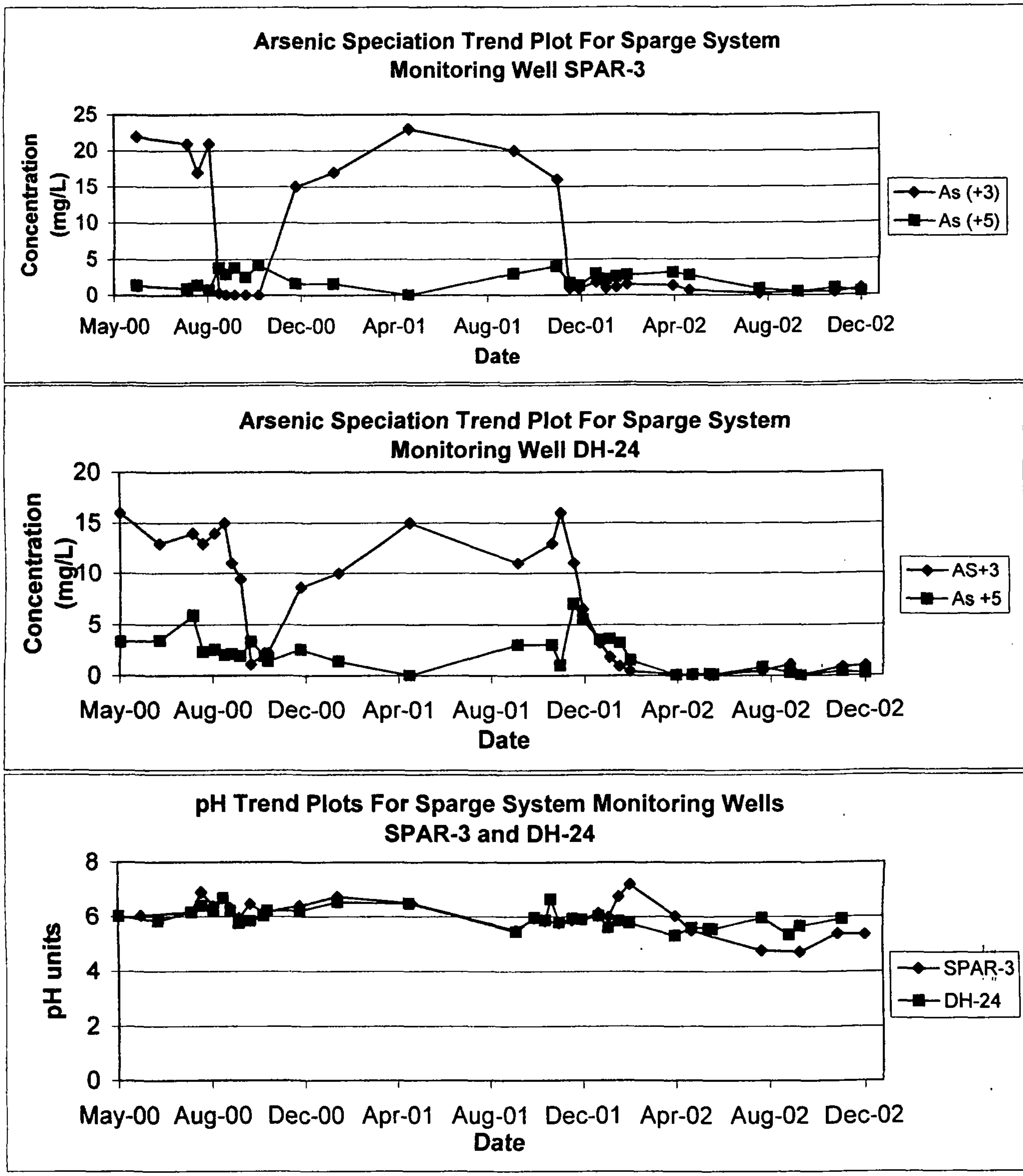


FIGURE 4-4. PHASE III WATER QUALITY TREND GRAPHS FOR SPAR-3 AND DH-24

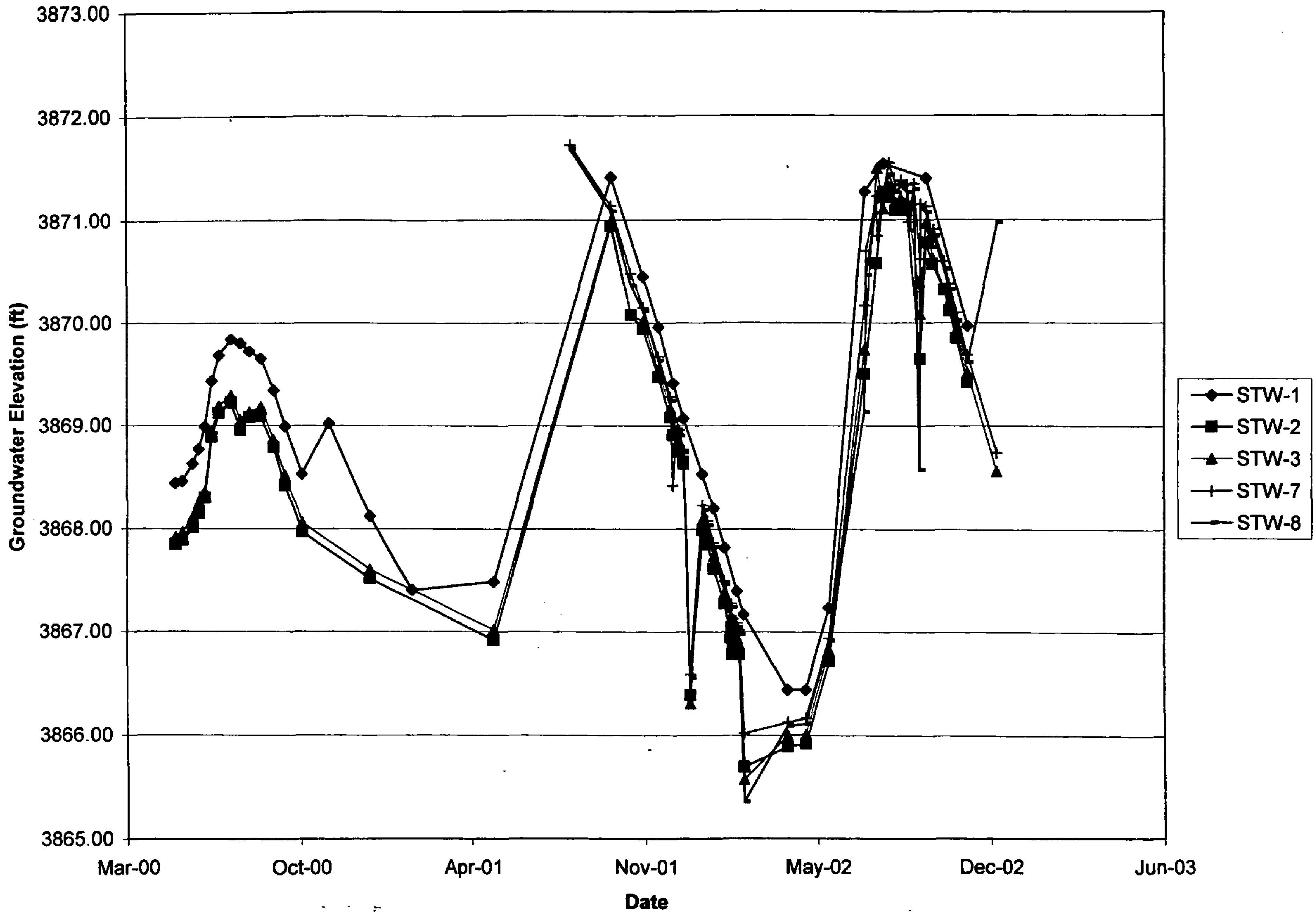


Figure 4-5. Water Level Trends at Upgradient Wells at SPAR-1 & SPAR-2 Sparge System

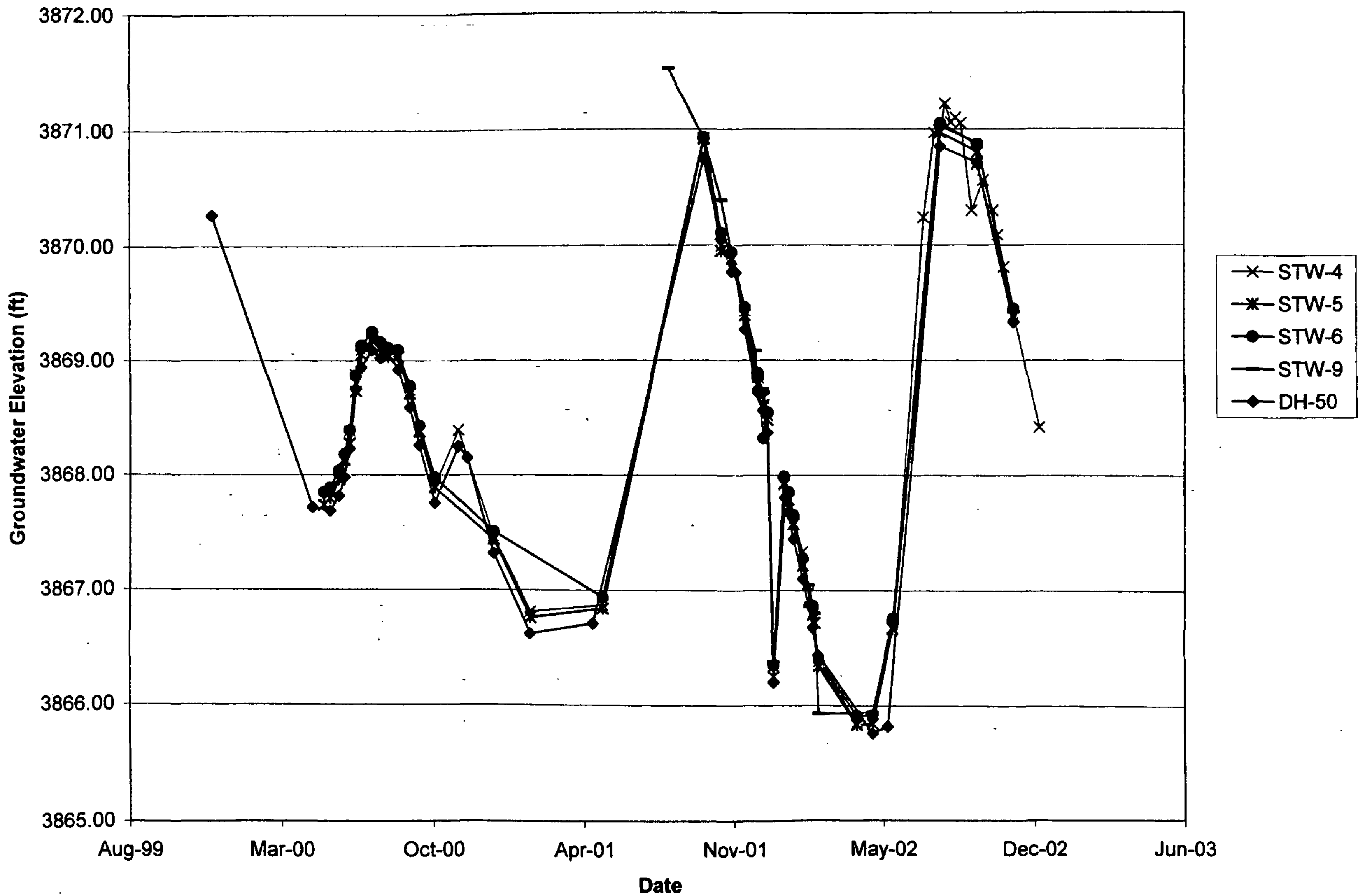
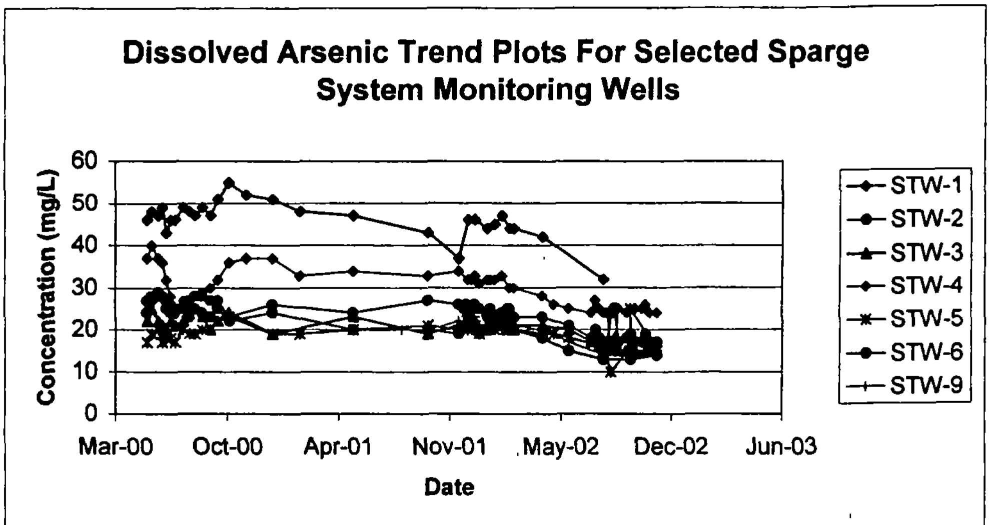
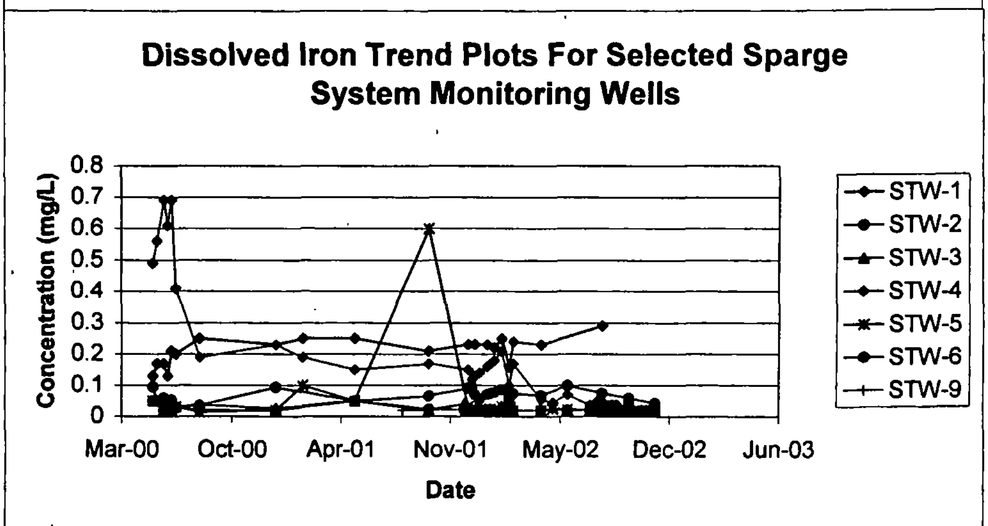


Figure 4-6. Water Level Trends at Downgradient Wells at SPAR-1 & SPAR-2 Sparge System





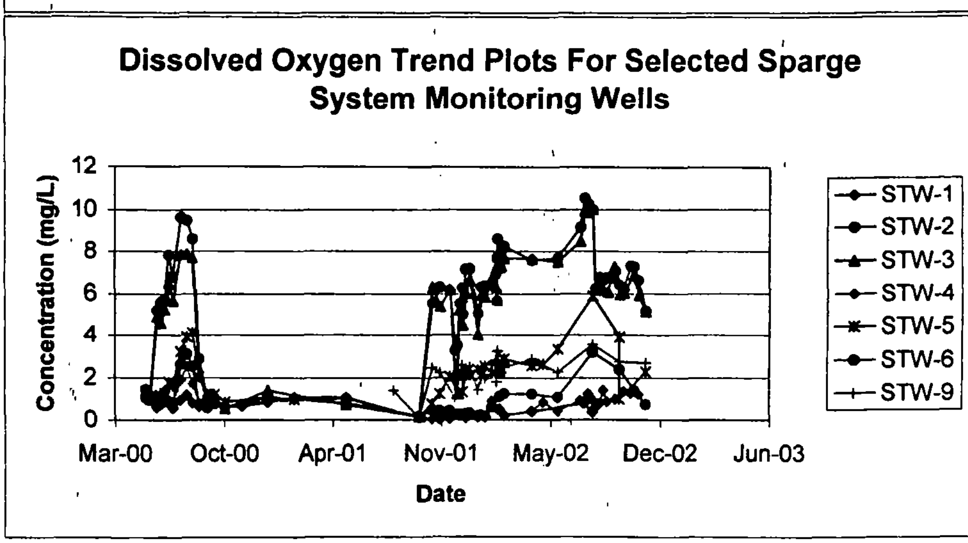
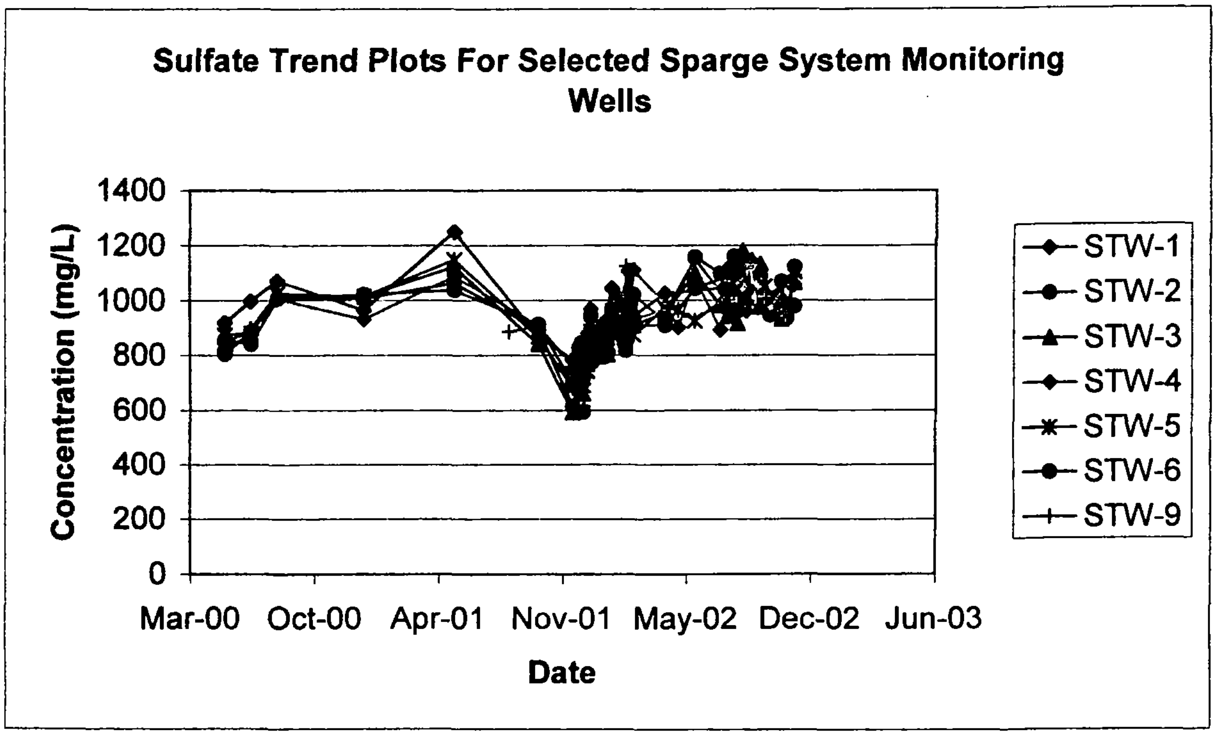


FIGURE 4-7. PHASE III WATER QUALITY TREND GRAPHS FOR STW-1 THROUGH STW-6 AND STW-9



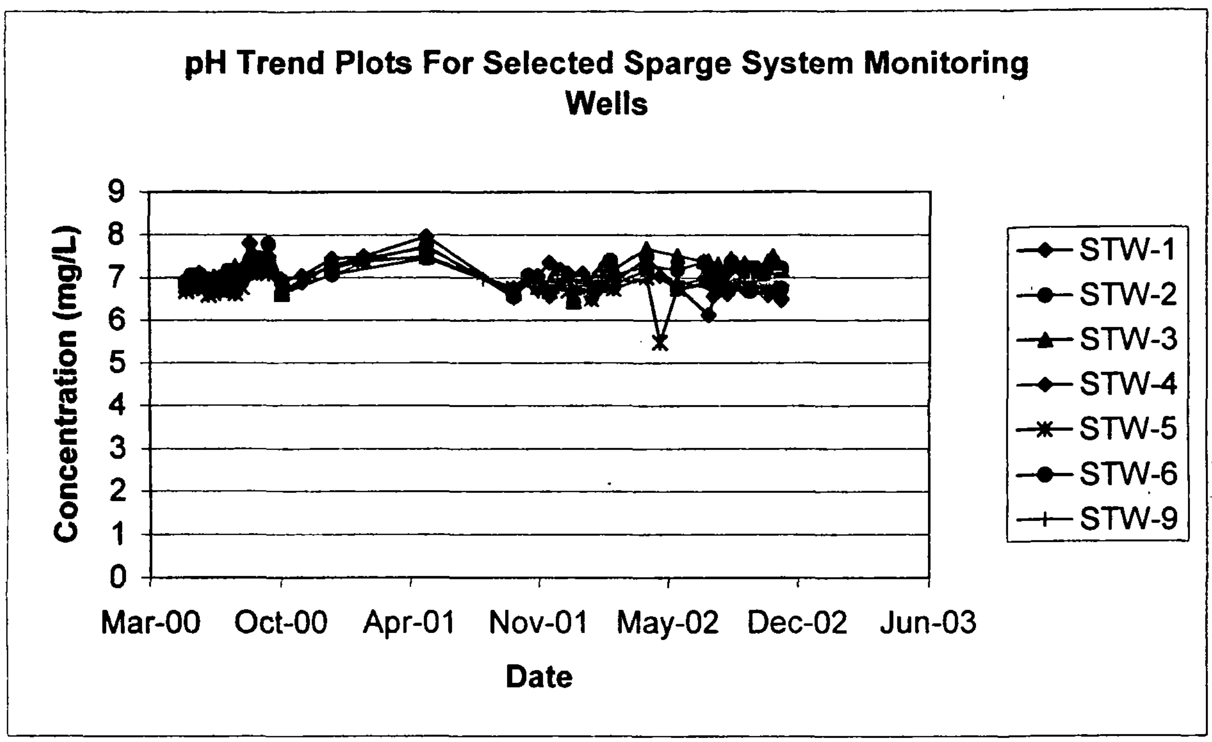
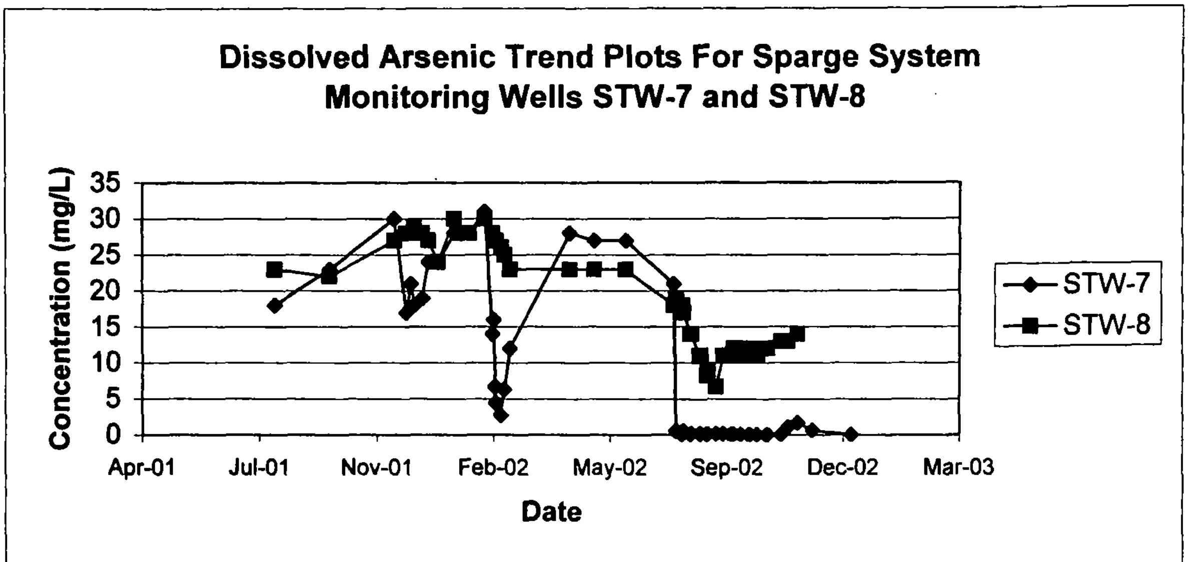
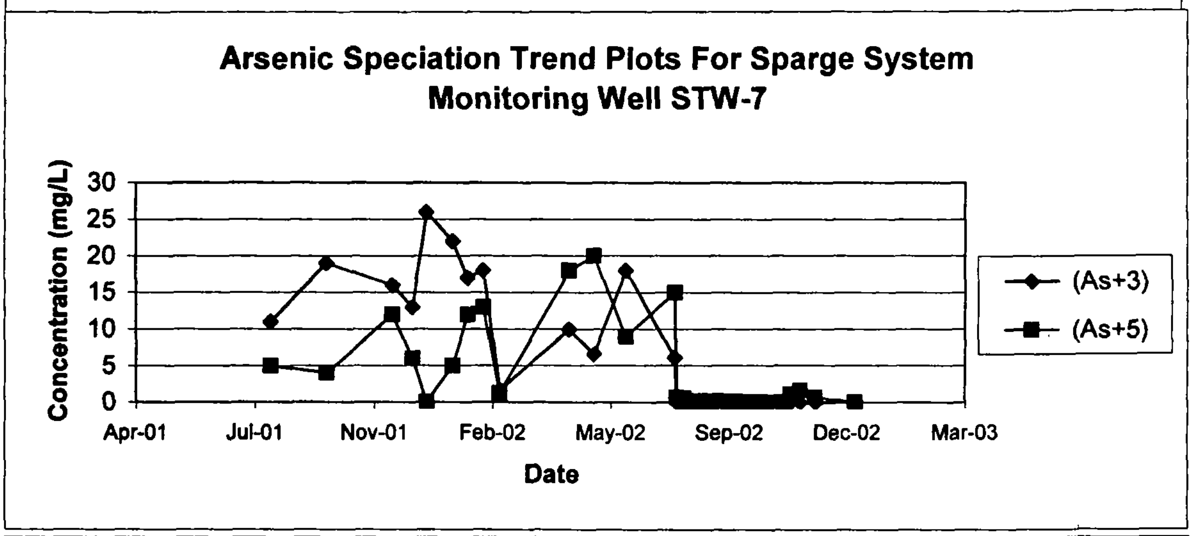


FIGURE 4-8. PHASE III WATER QUALITY TREND GRAPHS FOR STW-1 THROUGH STW-6 AND STW-9





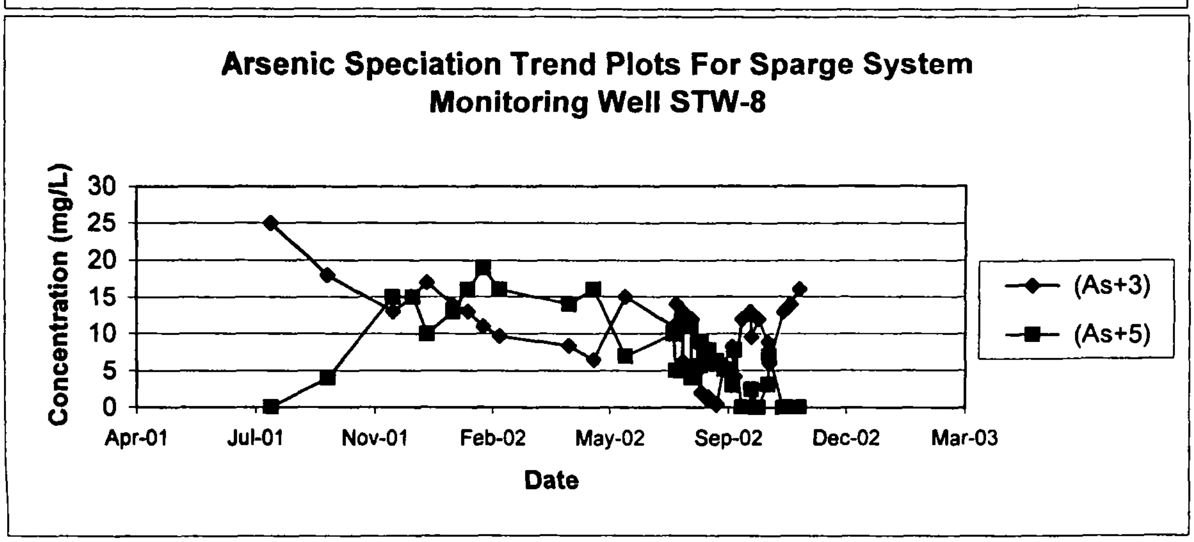
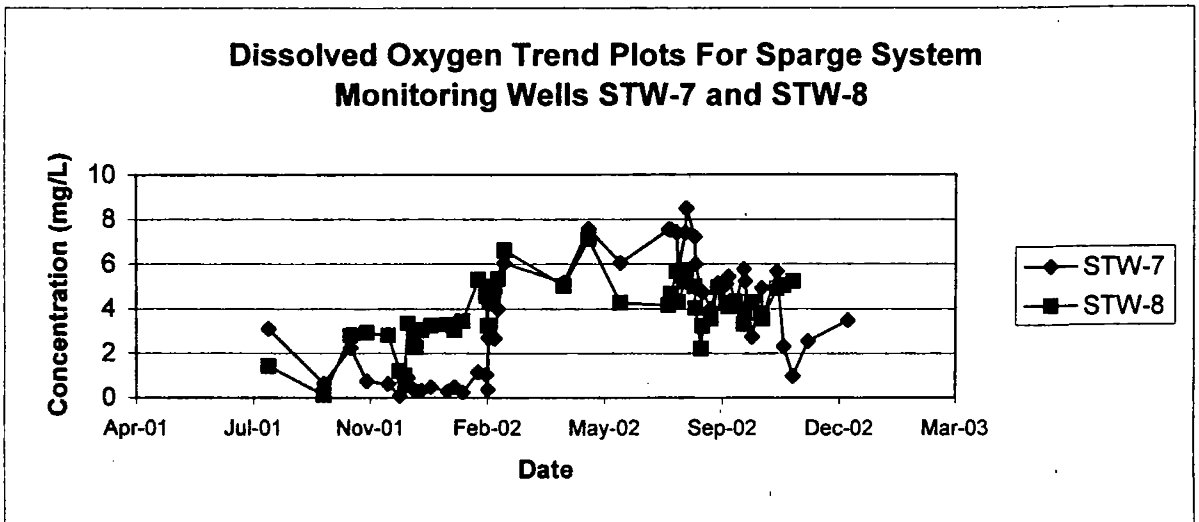
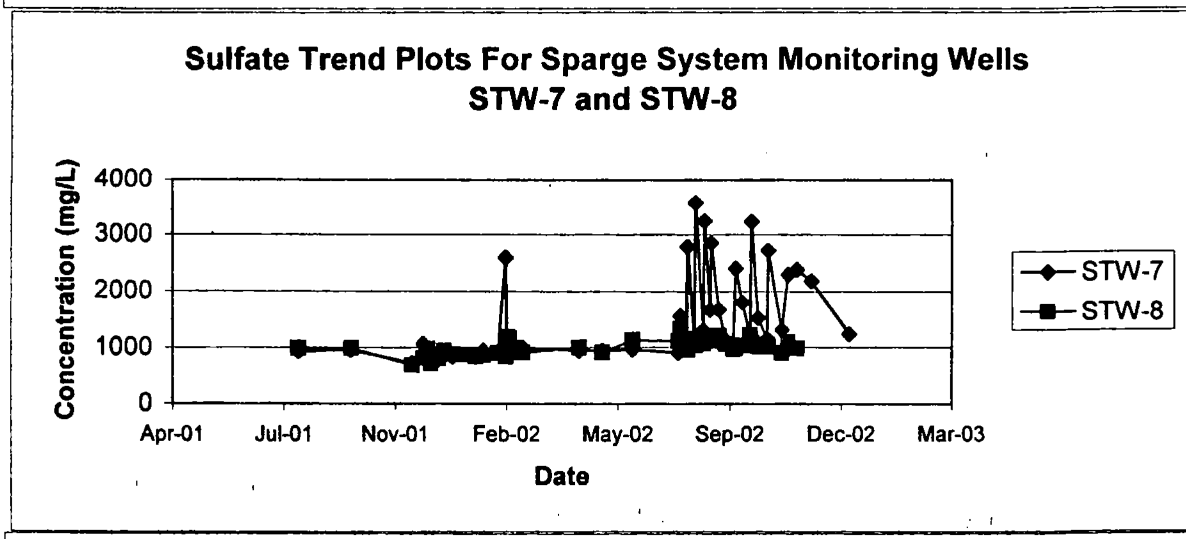


FIGURE 4-9. PHASE III WATER QUALITY TREND GRAPHS FOR STW-7 AND STW-8





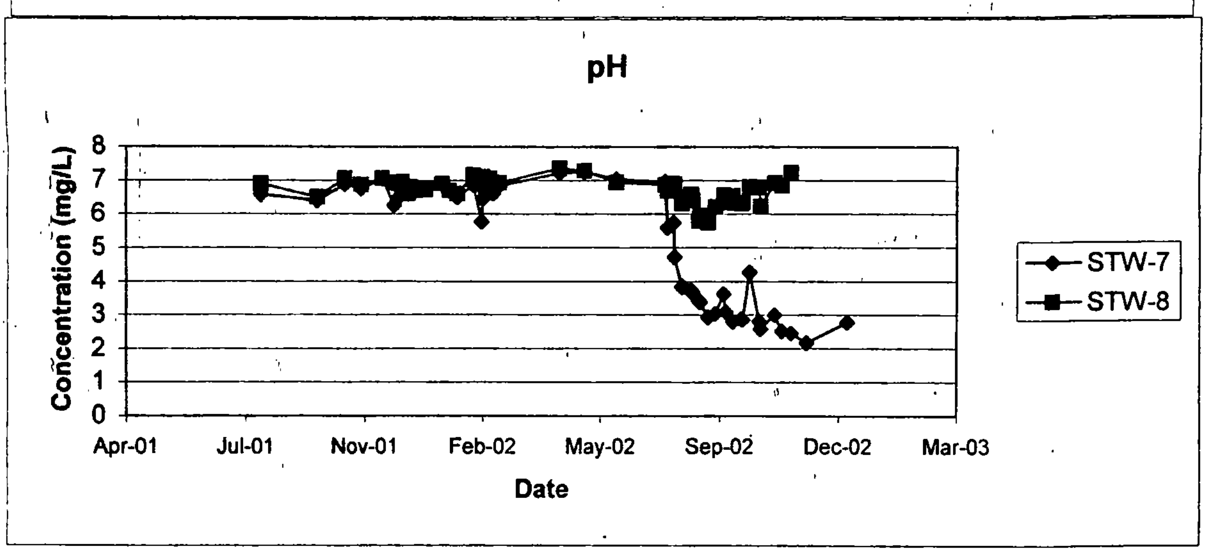
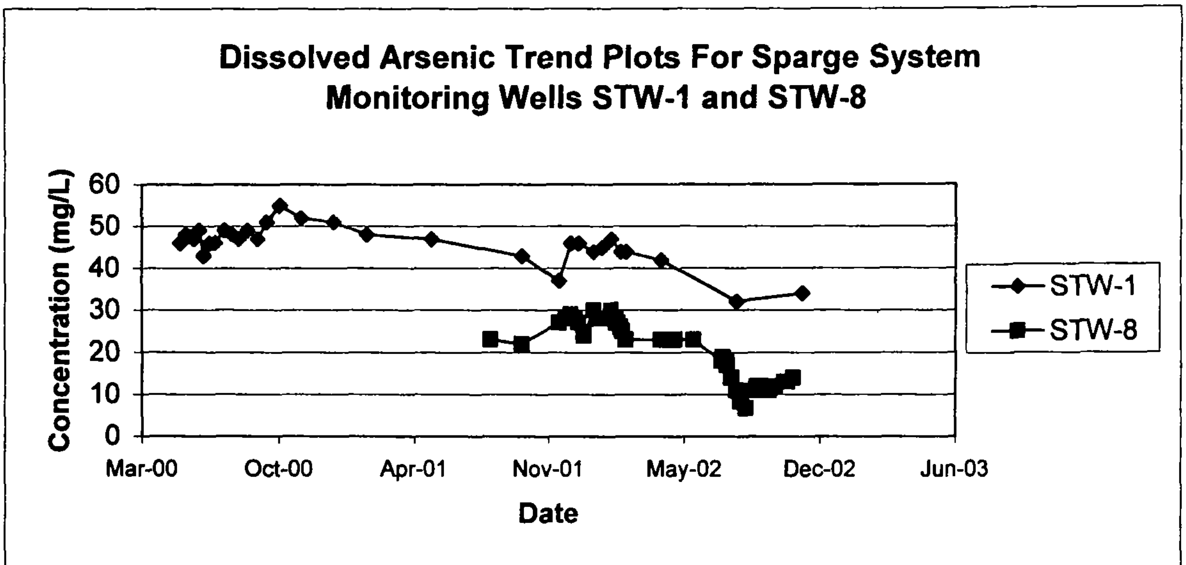
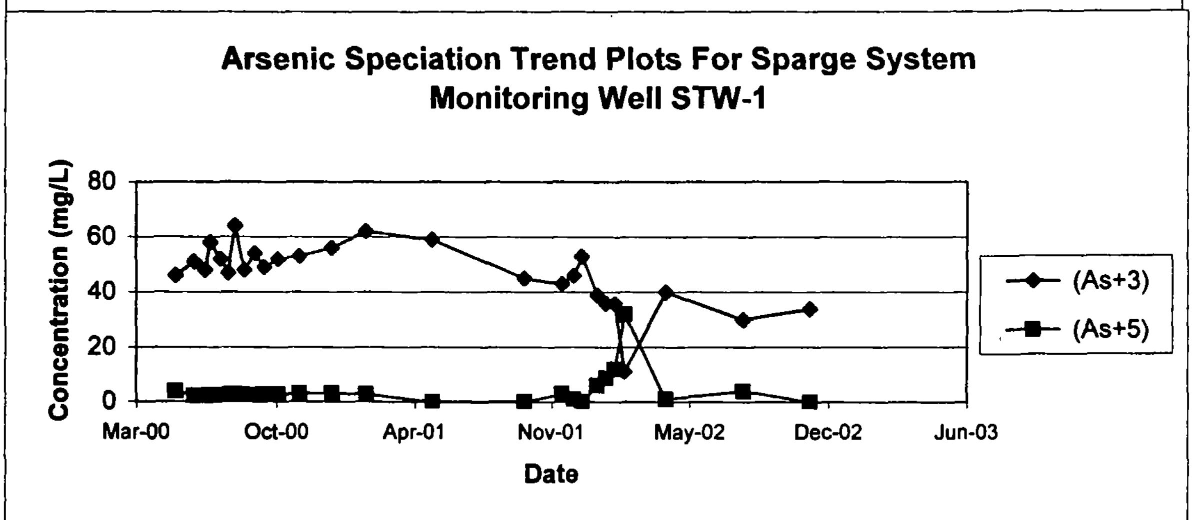


FIGURE 4-10. PHASE III WATER QUALITY TREND GRAPHS FOR STW-7 AND STW-8





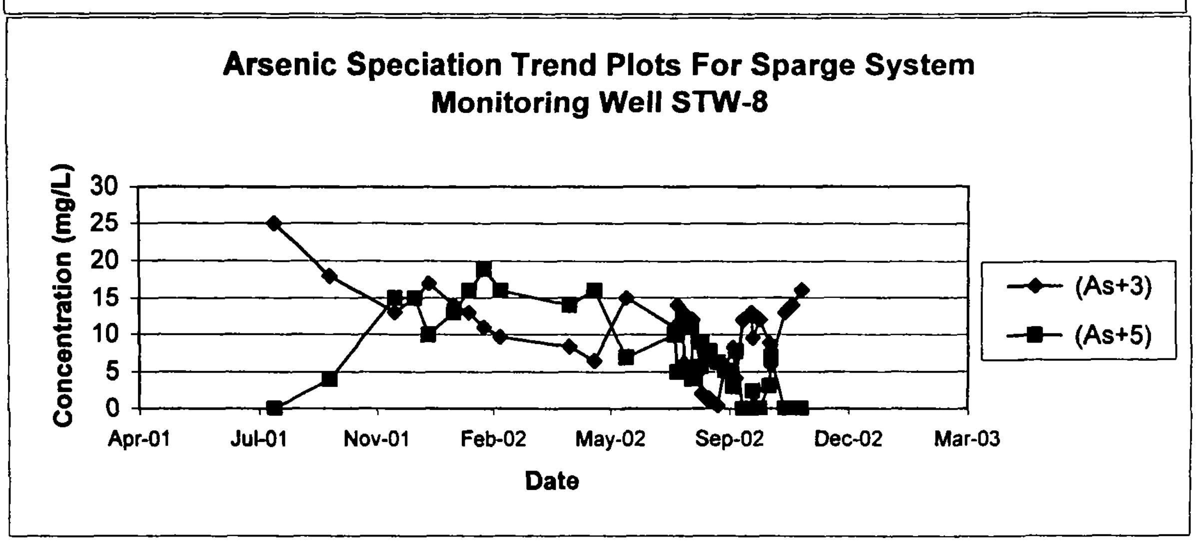
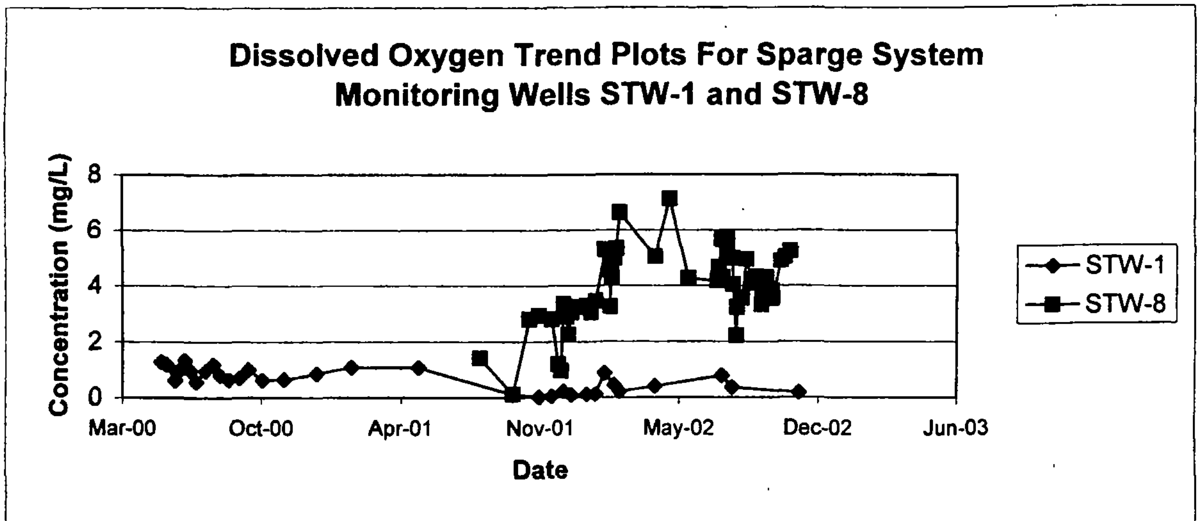
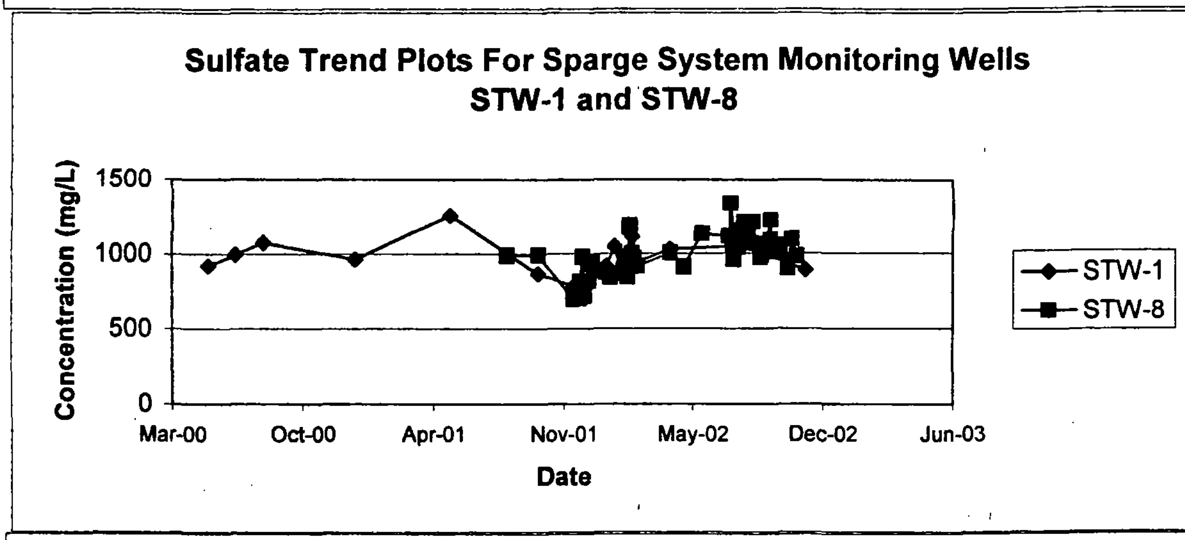


FIGURE 4-11. PHASE III WATER QUALITY TREND GRAPHS FOR STW-1 AND STW-8





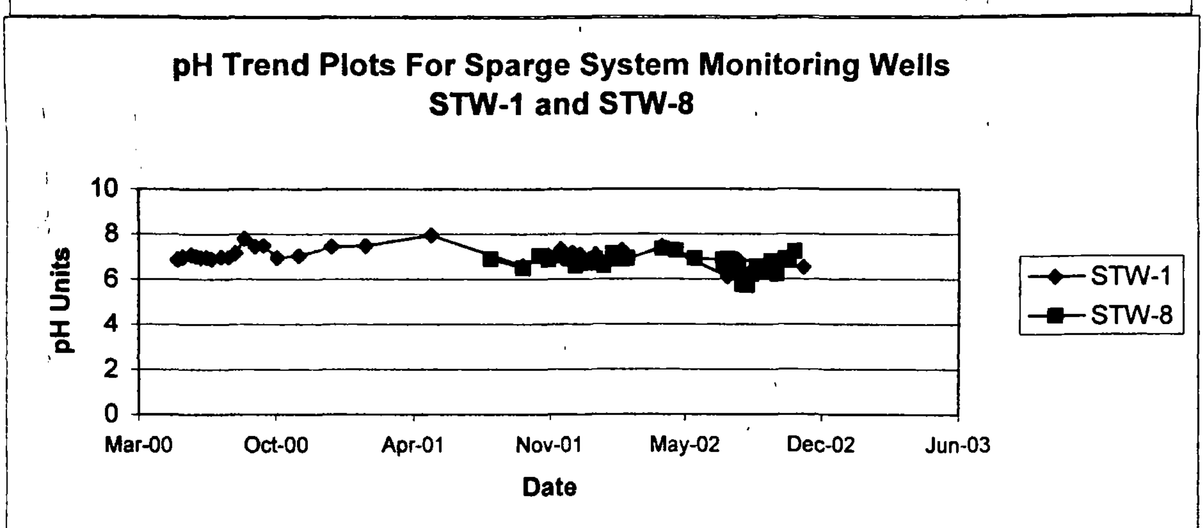


FIGURE 4-12. PHASE III WATER QUALITY TREND GRAPHS FOR STW-1 AND STW-8

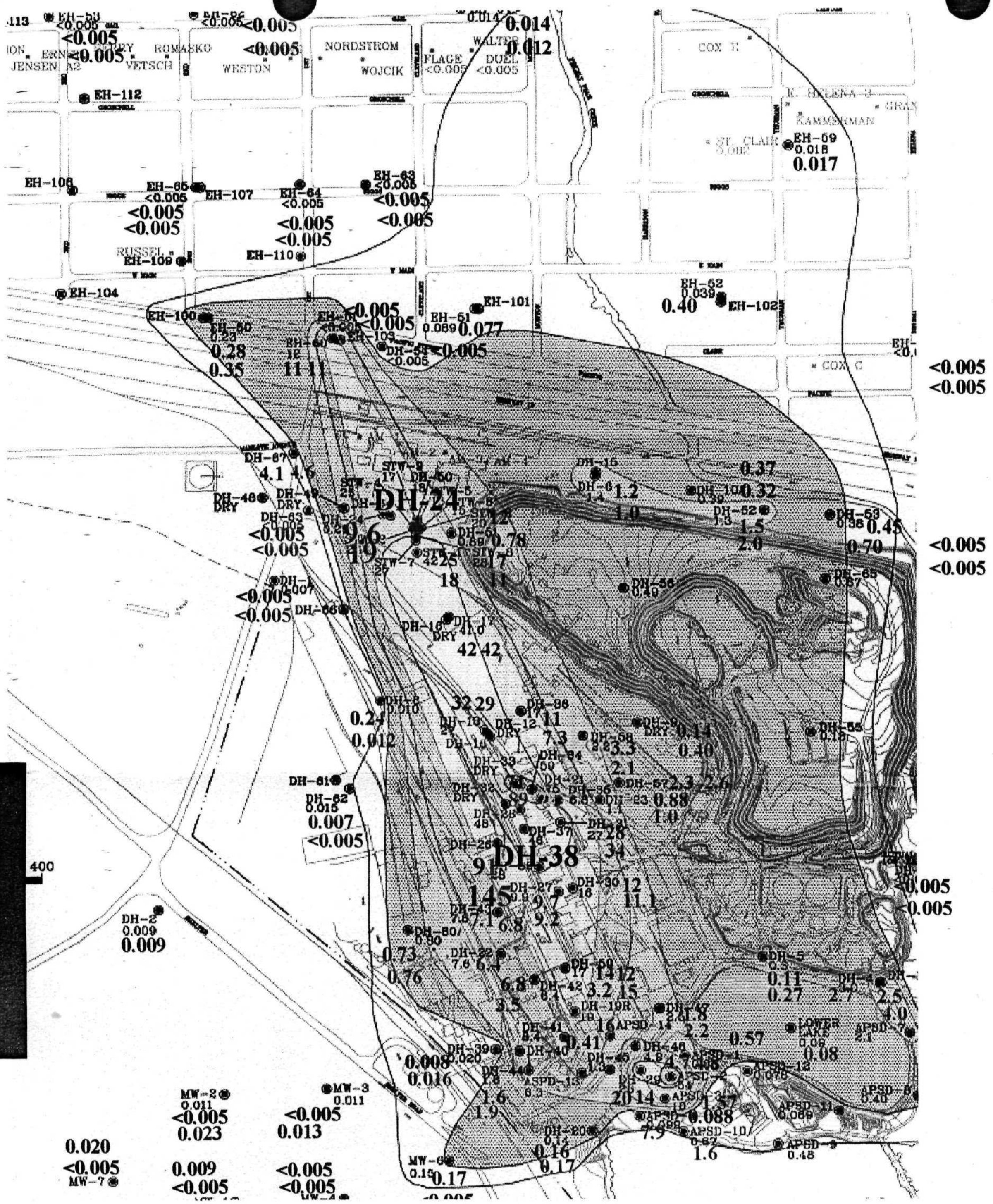


Figure 5-1

Shallow Aquifer May/June 2003 Arsenic Concentrations (Red Values) and June 2004 Concentrations (Blue Values) On May 2002 Plume Map